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1958

WATER SORPTION PROPERTIES OF HOMOIONIC CLAY MINERALS

W. Arthur White

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JOHN C. FRYE, *Chief* URBANA, ILLINOIS

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WATER SORPTION PROPERTIES OF HOMOIONIC CLAY MINERALS

W. ARTHUR WHITE

ABSTRACT

In order to understand better the fundamental factors that control the properties of clay-water systems, water sorption properties of seven groups of clay minerals (montmorillonite, attapulgite, illite, kaolinite, halloysite, diaspore, and gibbsite) were studied by means of Atterberg plastic limits, slope of the liquid limit line, and water sorption.

The data indicate that the structure of the clay mineral is primary and that exchangeable cations are secondary in determining the water adsorption and plastic properties of clay minerals and clay-water systems.

Sodium gave higher plastic values than did any of the other cations except lithium for the montmorillonites, whereas it gave lower values than did the other cations for the illites, kaolinites, halloysites, diaspores, and gibbsites. In addition, sodium gave the highest water-sorption values of any of the cations for the montmorillonites, whereas it gave values no higher than did the other cations for the other clay mineral groups.

The angle of slope of the liquid limit line is probably a measure of the thixotropic properties of a clay mineral.

The characteristics of the water sorption curves tend to reflect the structure and properties of the clay minerals.

INTRODUCTION

This investigation of the water sorption and plastic properties of clay-water systems, using homoionic clay minerals, was undertaken to obtain a better understanding of the fundamental factors that control the properties of clay-water systems.

According to the clay mineral concept (Grim, 1940a) that is generally accepted, ". . . clay materials are composed essentially of crystalline particles of members of any one or more of a few groups of minerals known as the 'clay minerals.' The clay minerals are hydrous aluminum silicates, frequently with some replacement of the aluminum by iron and magnesium and with small amounts of alkalies and alkali-earths. In rare instances magnesium and iron completely replace the aluminum."

Data on the attributes of clay mineral—water systems are of fundamental importance in clay mineral research. Information concerning the relationship of the clay-water systems and the properties of clays should be of value, first, to the geologist working on engineering problems, enabling him to predict the behavior of clay-containing sediments he might encounter; second, to the economic geologist, enabling him to determine more accurately the specific economic uses of a clay; and third, to the geologist working on structural, sedimentational, and environmental problems.

The information should also give to the soil engineer a better understanding of the behavior to be expected from deposits of clay material with, on, and through which buildings are to be constructed. In addition, the ceramist could use such data to predict with more certainty the properties of a new clay deposit, enabling him, with a minimum of waste, to improve the quality of his ware or to develop a new mix that has the desired properties.

This report is adapted from a doctoral dissertation completed at the University of Illinois, based on research work done at the Illinois State Geological Survey.

The author wishes to express his appreciation to Professor R. E. Grim for his inspiration and guidance, to Professors G. W. White, H. R. Wanless, G. L. Clark, and C. A. Chapman, all of the University of Illinois, for their advice and suggestions.

PREVIOUS WORK

Literature on the various phases of clay-water systems is extensive, but here only a few contributions are mentioned briefly to serve as background for this investigation.

Atterberg (1911, p. 4) introduced the Atterberg plastic limits as a means of classifying the agricultural soils in Sweden and of studying their differences in physical properties, but the limits were not used extensively until Terzaghi (1925, p. 20) realized their value in studying the engineering properties of soils.

Grim (1940b, p. 216) was one of the first investigators to bring to the attention of the engineers the fact that clay minerals are the components of soils or argillaceous rocks and in large degree control the physical properties of the soils.

White (1947, p. 54), using the Atterberg limits with purified clay minerals, showed that each group of clay minerals (illites, montmorillonites, etc.) has plastic limits that are characteristic of the group; and Grim (1948, p. 8) showed that by treating clay materials with sulfuric acid, phosphoric acid, and sodium hexametaphosphate, the plastic properties can be changed.

Winterkorn and Baver (1934, p. 291) were among the first soil scientists to study the water sorption properties of agricultural soils; and Endell et al. (1938, p. 15) were the first to study the water sorption properties of individual clay minerals.

An x-ray study of montmorillonites by Hofmann et al. (1933, p. 340) showed that montmorillonites swell in the presence of moisture. Later, Bradley et al. (1935, p. 216), by means of x-ray analysis, found that hydrogen montmorillonite adsorbs water stepwise, a layer at a time, until as much as four water layers have been adsorbed, and that the number of molecular water layers adsorbed depends on the relative humidity of the environment. Hendricks and Jefferson (1938, p. 863) suggested that the first layers of water are rigid with a structure similar to that of ice and that the ice-like structure is hydrogen-bonded to the tetrahedral layers (silica layers) of the montmorillonite.

Later, Hendricks et al. (1940, p. 1457), by means of differential thermal analyses and x-ray data, postulated that the exchangeable cations on the surface of montmorillonites treated with calcium or magnesium hydrate with six molecules of water; cations on the surface of montmorillonites treated with lithium hydrate with three molecules of water. After the cations have completed hydration, the surface of the montmorillonite continues hydration. In the case of the sodium, potassium, and hydrogen montmorillonites, only the surface hydrates.

Norrish (1954, p. 256), from an x-ray investigation of the water sorption of montmorillonites in various concentrations of chloride salts of hydrogen, lithium, sodium, calcium, magnesium, potassium, and ammonium, found that lithium and hydrogen montmorillonites adsorb water stepwise until four molecular layers of water have been adsorbed. Then there is a jump of nine molecular layers, after which water sorption is stepwise again. Similar behavior is true of sodium montmorillonite, except that after three molecular water layers have been adsorbed, there is a jump of ten molecular water layers before water sorption is stepwise again. Norrish also found that calcium and magnesium montmorillonites take up two molecular water layers at once, and then a third, but he did not notice any further water sorption. The potassium and ammonium montmorillonites did not expand beyond two water layers unless sodium was introduced.

Grim (1948, p. 8) postulated that oriented water develops outward from all basal planes of clay minerals. The first few water layers are rigid, but with increasing amounts of adsorbed water a thickness is reached where the water has imperfect or no orientation. After enough water has been put into the system to fill the rigid water requirements, only a small amount of water need be added to develop plasticity.

DEFINITIONS

Plasticity, according to Grim (1953, p. 1), is "the property of material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed." In clays plasticity develops when small amounts of water are added.

Dilatancy is the property of certain clay-water systems in which the resistance to shear increases at a greater rate than the increase in the rate of shear; that is, a dilatant clay-water system is one in which the moist clay resists being molded into shape when shearing forces are applied rapidly, but which will flow slowly under its own weight if allowed to stand.

Thixotropy is the property of a clay-water system which causes it to undergo a gel-to-sol-to-gel transformation upon agitation and subsequent rest (Fischer and Gans, 1946, p. 288).

Atterberg limits of a soil or clay are the liquid limit, plastic limit, and plastic index. Allen (1942, p. 263) defines them as follows:

1) "Liquid limit is the moisture content, expressed as a percentage by weight of the oven-dry soil, at which the soil will just begin to flow when jarred slightly."

2) "Plastic limit is the lowest moisture content, expressed as a percentage by weight of the oven-dry soil, at which the soil can be rolled into threads $\frac{1}{8}$ inch in diameter without breaking into pieces. Soils which cannot be rolled into threads at any moisture content are considered non-plastic."

3) "Plastic index is the difference between the liquid limit and the plastic limit . . . It is the range of moisture content through which a soil is plastic. When the plastic limit is equal to or greater than the liquid limit, the plastic index is recorded as zero."

Water sorption is absorption and adsorption by physical and chemical means.

1) Absorption of water is the taking up of water by capillary suction.

2) Adsorption of water is the adhesion of water molecules to the surface of the clay minerals by bonding processes.

MATERIALS

Fourteen samples of seven different groups of clay minerals (attapulgite, montmorillonite, illite, kaolinite, halloysite, diaspore, and gibbsite) were selected as representative of various clay mineral groups and as illustrative of variations within the group. The fourteen samples are as follows:

1) Montmorillonite 1, from Pontotoc, Mississippi, is a high-iron montmorillonite (table 1) with some substitution of Al^{+++} for Si^{++++} (personal communication, R. E. Grim). It is used as a bonding clay for molding sand and, after acid treatment, for removing color from oil. The exchangeable cations are calcium and hydrogen, and the cation exchange capacity is 93 me/100 gm. (Grim and Cuthbert, 1945a, p. 10). Montmorillonite 1 does not swell appreciably in water.

2) Montmorillonite 2, from Cheto, Arizona, is a low-iron montmorillonite (table 1) with little substitution of Al^{+++} for Si^{++++} (personal communication, R. E. Grim). It is used for the manufacture of catalysts and as a bleaching clay after acid treatment. Calcium is the chief exchangeable cation, and the cation exchange capacity is about 130 me/100 gm. Montmorillonite 2 does not swell appreciably when placed in water.

3) Montmorillonite 3, from Belle Fourche, South Dakota, has a slightly higher aluminum content than do the other montmorillonites. Some aluminum is replaced by magnesium, but very little is replaced by iron (personal communication, R. E. Grim). Sodium is the exchangeable cation (Grim and Cuthbert, 1945a, p. 10). There is some substitution of Al^{+++} for Si^{++++} (Greene-Kelley, 1953, p. 53). The clay has a cation exchange capacity of 93 me/100 gm. (Grim and Cuthbert, 1945a, p. 10) and swells in water to several times its volume. Its thixotropic properties make it well suited for use as a drilling mud; it is also used as a bonding clay for molding sands in foundries.

4) Montmorillonite 4, from Olmsted, Illinois, is a natural fuller's earth containing about 4 percent less aluminum than do the other montmorillonites studied, with iron and magnesium filling the octahedral positions not filled by aluminum. The cation exchange capacity is low for montmorillonite, 37 me/100 gm. (compared

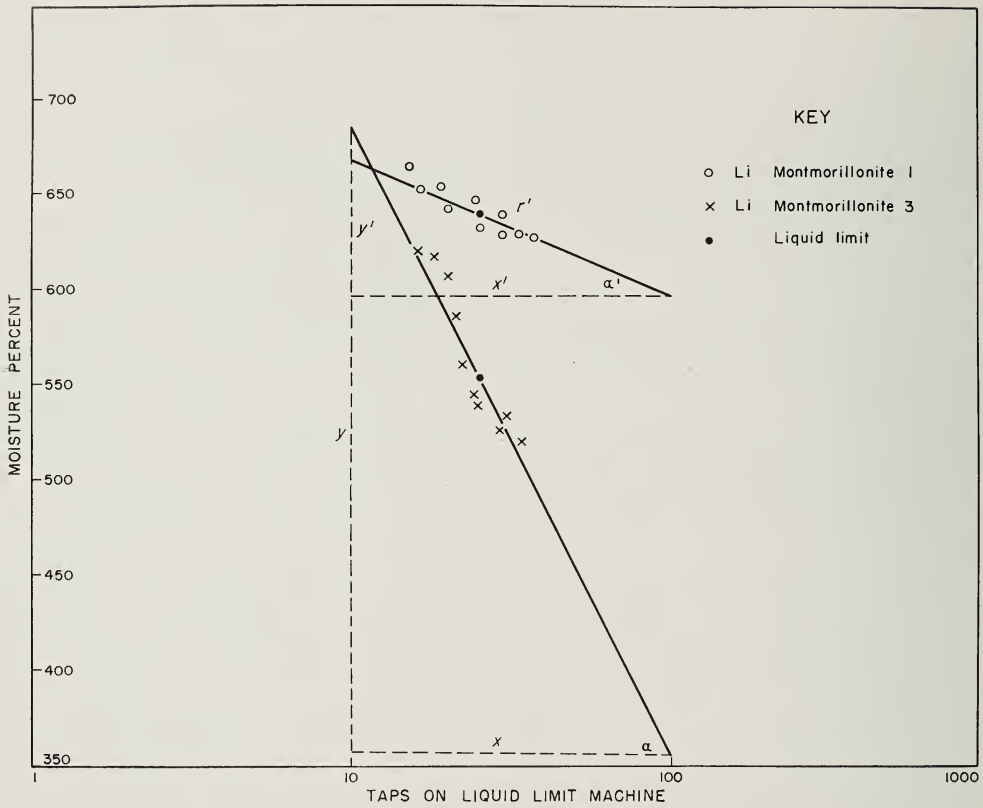

Fig. 1.—Method of obtaining slope of the liquid limit line.

with 93, 130, and 93 me/100 gm., respectively, for montmorillonites 1, 2, and 3). The exchangeable cations are calcium, magnesium, and hydrogen. The clay is slightly acidic. This montmorillonite differs from the others in that it was probably transported and deposited as montmorillonite instead of being a devitrification product of volcanic ash. Like montmorillonites 1 and 2, montmorillonite 4 does not swell appreciably when placed in water.

5) Attapulgite, from Quincy, Florida, is a natural fuller's earth and a member of the sepiolite-palygorskite group.

6) Illite 1, from Fithian, Illinois, is typical of illites found in most sediments. Calcium and magnesium are the chief exchangeable cations, although there are some exchangeable hydrogen cations. The cation exchange capacity is 28 me/100 gm.

7) Illite 2, from Jackson County, Ohio, is more coarse-grained, contains more iron, and is less plastic than illite 1. The sample also contains a chlorite-type clay material. The cation exchange capacity is a little less than that of illite 1.

8) Illite 3, from Morris (Goose Lake), Illinois, contains less potassium than does illite 1. It has a cation exchange capacity of 31 me/100 gm., with more hydrogen and less magnesium as exchangeable cations. The pH indicates that the clay is very acid. It is an excellent bonding clay for synthetic molding sands.

9) Kaolinite 1, from near Anna, Illinois, is a very plastic kaolin with a particle size 85 percent less than 0.5 micron. This kaolinite is poorly crystallized, indicating that irregular shifts b/3 are present in the lattice. The cation exchange capacity is about 18 me/100 gm.

10) Kaolinite 2, from Dry Branch, Georgia, is a coarse-grained and well crystallized kaolinite without much plasticity. It is somewhat more refractory than is kaolinite 1 and has a lower cation exchange capacity.

11) Halloysite 1, from Eureka, Utah, is a halloysite ($2H_2O$) with a cation exchange capacity of 12 me/100 gm. Electron micrographs show the presence of tubes, many of which are split.

12) Halloysite 2, from Bedford, Indiana, is a halloysite ($4H_2O$) with a cation exchange capacity of 9 me/100 gm. It contains more water and has a lower cation exchange capacity than does halloysite 1. The exchangeable cation for both halloysites is calcium.

13) Diaspore, from Swiss, Missouri, is a high-alumina, nonplastic clay used in the refractory industry.

14) Gibbsite, from a bauxite deposit near Irvington, Georgia, contains less aluminum and is somewhat more plastic than the Missouri diaspore.

ANALYTICAL PROCEDURE

Purification of Clay Minerals

Because most clays contain nonclay minerals as well as clay minerals, it is necessary to remove as large a percentage of the impurities as possible to obtain results representative of the particular clay minerals. As a large percentage of the nonclay minerals have an average diameter greater than one micron in equivalent spherical diameter, and most of the clay minerals have average diameters less than one micron, it frequently is possible to separate them by a sedimentation method.

In this investigation the clay minerals were purified by placing about 20 pounds of crude clay in a 10-gallon crock and washing it with distilled water until the clay dispersed. The clay suspensions were then allowed to settle according to Stokes' law, and a clay-size fraction ranging up to approximately 1 micron was siphoned into another 10-gallon crock. The water was removed from the less-than-one-micron clay fraction by sucking the water from the clay through unglazed porcelain filter cones under vacuum, after which the clay was air-dried.

Preparation of Homoionic Clay Minerals

Homoionic clay samples were prepared by leaching 150-gram batches with 1 liter of neutral 2N salt solutions of ammonium acetate and potassium, sodium, lithium, calcium, and magnesium chlorides. The clays were then washed free of the salt solutions with distilled water. Several homoionic samples, selected at random, were leached with 2N ammonium acetate and the exchangeable cations were determined to ascertain completeness of replacement of the desired cation. Chemical analyses of the filtrates indicated that about 90 percent of the original cations had been replaced.

Experimental Methods

To study the clay mineral—water properties of the homoionic clay minerals, the plastic and liquid limits (known as the Atterberg limits and almost universally used at the present time for determining plasticity), the slope of the liquid limit line, and water sorption of the clay minerals were investigated.

Atterberg Limits

Plastic limits.—The Atterberg plastic limits were determined by rolling balls of clay at decreasing moisture contents until that moisture content was reached at which a thread 1/8 inch in diameter just began to crumble.

Liquid limits.—The liquid limits were determined by the method described by Casagrande (1932, p. 122). The sample, consisting of clay mineral and water, was placed in the cup of the Casagrande liquid limit machine, and a groove 2 mm. wide at the base, 11 mm. wide at the top, and 8 mm. deep was made in the sample. The cup was then dropped 1 cm. as many times as were required to cause the clay to flow together for at least 1/4 inch. Samples with 10 different moisture contents requiring from 15 to 35 taps were run.

The moisture content was plotted on semilogarithmic paper along the arithmetic scale (ordinate), and the taps were indicated on the logarithmic scale (abscissa). A straight line was drawn through these points; the moisture content at the point where the lines cross the 25-tap line is considered the liquid limit.

In preparing montmorillonite for liquid limit determinations, it has been found (White, 1949, p. 509) that the water cannot be added as with other clays, that is, by adding increasing amounts of water. The process must be started with dilute suspensions, the water allowed to evaporate, and the suspension stirred every few hours to insure an even moisture distribution.

Slope of the Liquid Limit Line

The slope of the liquid limit line is herein defined as the angle, α, which the line plotting taps versus moisture content makes with the horizontal (fig. 1). To obtain angle α, the liquid limit line, r, is extended until it intersects the 10- and 100-tap lines. A line, x, is drawn perpendicular to the 10-tap line with its origin at the point where the liquid line, r, intersects the 100-tap line. Using the 10-tap line, y, as the tangent of the angle α, which intersects both lines x and r forming a right triangle, angle α can be obtained by the equation

$$\tan \alpha = \frac{y}{x}$$

in which $\tan \alpha$ is the angle of slope, x is 100–10 taps (90 taps), and y is the difference in moisture content between the points where the line x and the hypotenuse r cut the tangent y.

The angle of slope of the liquid limit line appears to be related to the thixotropy at the liquid limit. The steeper the slope, the greater the ability of the clay mineral to set into a gel.

Water Sorption

Water sorption apparatus used in this investigation was similar to that used by Enslin (1933, p. 147). It consisted of a 3-way stopcock, funnel, U-tube, porous filter, a male and a female ground-glass joint, and a 5 ml. pipette, as illustrated in figure 2.

Before running an adsorption analysis, the funnel was filled with water which

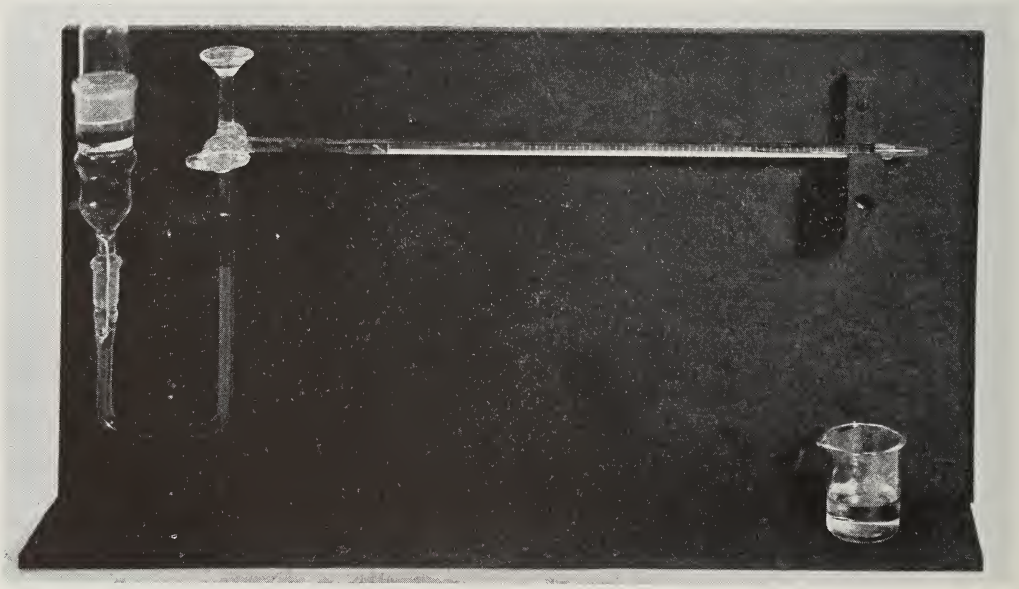

Fig. 2.—Enslin water sorption apparatus.

was allowed to flow through the U-tube until it made contact with the porous plate. As much air as possible was forced from under the porous plate to give maximum surface contact with the liquid. The pipette was filled until the meniscus of the water along the top side read about 4 ml. The stopcock was turned so that there was a water contact between the pipette and the U-tube. Evaporation curves of the homoionic clay minerals were determined by taking readings, beginning with 15 seconds and doubling the time between successive readings, until about two days had passed.

Because clays of different particle sizes give different sorption curves (Pichler, personal communication), the samples were ground and the 120- to 230-mesh material was selected for analysis.

The moisture content of the clay was then determined, and calculations were made to find the amount of air-dried clay that would equal ½ gram of oven-dried clay (the amount used).

The clay was poured into the Enslin sorption apparatus against a spatula so that it would be fairly evenly distributed over the surface of the porous plate. The ground-glass joint was tapped with the spatula to level off the ridges, and the cover was placed over the ground-glass joint to reduce evaporation to a minimum. Readings, to the nearest 0.01 ml., were taken from the pipette at 0, ¼, ½, 1, 2, 4, 8, 15, 30, 60, 120, 240, 480, 900, etc., minutes. The water-sorption time was plotted logarithmically and the adsorbed moisture was plotted arithmetically on semilogarithmic paper.

At the end of the sorption period, in order to check the accuracy of the method, the clay was taken from the Enslin apparatus and the moisture content was measured gravimetrically. The moisture as determined from the gravimetric method and the moisture as determined from the sorption curve were within small percentages of each other, the moisture as determined from the sorption curve generally being slightly higher. Evaporation curves were run with the sorption apparatus to determine the rate of water evaporation, and the water sorption data of the clay minerals were corrected to account for the water of evaporation.

In order to obtain water-sorption curves that are comparable, extreme care must be taken in making the determinations, and a definite procedure must be set up and followed rigidly.

If the packing is not the same for each clay, the curves will be different. Pichler (personal communication) has shown that the more material used to cover the same area, the lower will be the moisture content adsorbed per gram of material; that is, a gram of clay covering a given area will adsorb less than twice as much moisture as would be adsorbed by one-half of a gram of clay. (The sorption will be more rapid for the latter.) If one sample is leveled and another sample of the same material is left as it falls, their curves will be different, and the latter sample will adsorb less moisture. If two different particle sizes of the same clay are used, the coarser particle will adsorb more moisture and will adsorb it more rapidly.

Leaks around the stopcock will indicate more swelling than actually takes place, and water leaking from the funnel around the stopcock into the U-tube system will indicate less swelling than actually takes place. If the apparatus is not clean, the results will not be reliable because droplets of water may remain on the wall of the pipette and air bubbles cannot be dislodged. The evaporation loss should be checked from time to time.

ANALYTICAL DATA

Plastic Limits

The plastic limits for the clay minerals investigated (table 1) ranged from 20 for sodium diaspore to 124 for calcium attapulgite. White (1949, p. 508) found that the plastic limits for the clay minerals had the order: attapulgite>montmorillonite>illite >kaolinite.

Table 1.—Atterberg Plastic Limits

Clay Mineral	Adsorbed Cations					
	Ca^{++}	Mg^{++}	K^{+}	NH_4^{+}	Na^{+}	Li^{+}
Montmorillonite						
1	65	59	57	75	93	80
2	65	51	57	75	89	59
3	63	53	60	60	97	60
4	79	73	76	74	86	82
Attapulgite	124	109	104	97	100	103
Illite						
1	40	39	43	42	34	41
2	36	35	40	37	34	38
3	42	43	41	39	41	40
Kaolinite						
1	36	30	38	34	26	33
2	26	28	28	28	28	28
Halloysite						
1	38	47	35	32	29	37
2	58	60	55	56	54	47
Diaspore	24	23	24	24	20	26
Gibbsite	25	27	25	22	26	26

In the present study, which includes more clay minerals, the proposed order is: attapulgite > montmorillonite > halloysite $(4H_2O)$ > illite > halloysite $(2H_2O)$ > kaolinite > gibbsite > diaspore. For the most part, the cations, other than sodium, had little effect on the plastic limits of the clay minerals. Sodium tended to give lower plastic limits than did the other cations for most of the clay minerals, but it tended to give a higher plastic limit for montmorillonite.

Montmorillonite

The plastic limits for the homoionic montmorillonites ranged from 51 for magnesium montmorillonite 2 to 97 for sodium montmorillonite 3, the order for the homoionic montmorillonites with various cations being $Na > NH_4 \leqq Li \leqq Ca > Mg \leqq K$ (table 1). The sodium montmorillonites had the highest plastic limits; calcium, magnesium, and potassium montmorillonites had the lowest (about equal). The ammonium montmorillonites were intermediate, and plastic limits for the lithium montmorillonites might be either high or low.

The plastic limits for homoionic samples of montmorillonite 4 varied less than those of the other three. Montmorillonite 4 had a variation of only 13 units between the high and low limits, whereas montmorillonites 1, 2, and 3 varied 36, 38, and 44 units, respectively.

All the homoionic montmorillonites 4, except sodium and ammonium montmorillonite, had higher plastic limits than did the corresponding homoionic montmorillonites 1, 2, and 3. Sodium montmorillonite 4 had a lower plastic limit than did sodium montmorillonites 1, 2, and 3. Ammonium montmorillonite 4 had a lower plastic limit than 1 and 2. At present there appears to be no logical explanation for montmorillonite 4 having higher plastic limits than the other homoionic montmorillonites for all the cations except sodium and ammonium. A possible explanation is that montmorillonite 4 contains illite and chlorite as impurities; but this explanation

does not appear very feasible, since both illite and chlorite have lower plastic limits than do the montmorillonites and would thus seem more likely, in a mixture with montmorillonite, to lower the plastic limits for *all* the cations. A more likely explanation may be that the illite, chlorite, and some of the montmorillonite occur as mixed-lattice clay minerals.

Calcium and sodium gave consistently higher plastic limit values than did magnesium and lithium, respectively. Ammonium tended to give higher limits than did potassium.

The plastic limits for the homoionic montmorillonites varied as follows: montmorillonite 1, $Na > Li > NH_4 > Ca > Mg \geqq K$; montmorillonite 2, $Na > NH_4 > Ca > Li > K > Mg$; montmorillonite 3, $Na > Ca \geqq NH_4 = K = Li > Mg$; and montmorillonite 4, $Na > Li > Ca > K \geqq NH_4 \geqq Mg$. (Where the sign $\geqq$ is used it means that one value is larger than another, but for all practical purposes they can be considered equivalent because they are within the range of experimental error.)

The boundary between the plastic state and the nonplastic state was not as sharp for sodium and lithium montmorillonites as it was for the other homoionic montmorillonites; therefore it was difficult to determine precisely the limit values for the sodium and lithium montmorillonites.

Attapulgite

The plastic limits ranged from 97 for ammonium attapulgite to 124 for calcium attapulgite, the order with the various cations being: $Ca > Mg > K = Li \geqq Na \geqq NH_4$. The divalent-cation attapulgites had higher plastic limits than did the attapulgites with monovalent cations. Plastic-limit values for the monovalent-cation attapulgites are so close together that they can be considered equivalent.

Illite

The plastic limits of the illites were lower than those of the montmorillonites, attapulgites, and halloysites ($4H_2O$), ranging from 34 for sodium illites 1 and 2 to 43 for magnesium illite 3 and potassium illite 1. This moisture range was much smaller than that of the montmorillonites and attapulgites and slightly smaller than that of the fine-grained kaolinites 1.

The plastic limits for the homocationic illites were: illite 1, $K \geqq NH_4 \geqq Li \geqq Ca \geqq Mg > Na$; illite 2, $K \geqq Li \geqq NH_4 \geqq Ca \geqq Mg \geqq Na$; illite 3, $Mg \geqq Ca \geqq K = Na \geqq Li \geqq NH_4$.

In all the illites, regardless of cation, the plastic limit was about 40 percent water, plus or minus a few percent, indicating that the character of the cation appears to have little influence on the plastic limits. Contrary to its action in the montmorillonites, sodium did not increase the plastic limits and in two of the illites actually lowered them.

Kaolinite

The kaolinites tended to have lower plastic limits than did the illites, montmorillonites, attapulgites, and halloysites, ranging from 26 for calcium kaolinite 2 and sodium kaolinite 1 to 38 for potassium kaolinite 1. Well crystallized, coarse-grained kaolinite 2 had a lower plastic limit than did the poorly crystallized, fine-grained kaolinite 1. In the coarse-grained kaolinite the cations had little, if any, effect on the plastic limits. In the poorly crystallized kaolinite there was an appreciable variation, the order with the various cations being: $K \geqq Ca \geqq NH_4 \geqq Li \geqq Mg > Na$.

Halloysite

The plastic limits of the halloysites ranged from those found in kaolinite 1 up into the range of the montmorillonites: 29 for sodium halloysite 1 ($2H_2O$) to 60 for magnesium halloysite 2 ($4H_2O$). The order for the various cations was: halloysite 1, $Mg > Ca \geqq Li \geqq K > NH_4 > Na$; halloysite 2, $Mg \geqq Ca \geqq NH_4 \geqq K \geqq Na > Li$, indicating higher limits for the divalent-cation than for the monovalent-cation halloysites.

The plastic limits of halloysite ($4H_2O$) were from 10 to 25 percent higher than those for halloysite ($2H_2O$). The latter contained about 15 percent less original moist-

Table 2.—Atterberg Liquid Limits

Clay Mineral	Adsorbed Cations					
	Ca^{++}	Mg^{++}	K^{+}	NH_4^{+}	Na^{+}	Li^{+}
Montmorillonite						
1	166	158	161	214	344	638
2	155	199	125	114	443	565
3	177	162	297	323	700	600
4	123	138	108	140	280	292
Attapulgite	232	179	161	158	212	226
Illite						
1	90	83	81	82	61	68
2	69	71	72	60	59	63
3	100	98	72	76	75	89
Kaolinite						
1	73	60	69	75	52	67
2	34	39	35	35	29	37
Halloysite						
1	54	54	39	43	36	49
2	65	65	57	61	56	49
Diaspore	31	31	33	32	27	42
Gibbsite	36	39	36	39	33	38

ure than did the former, which would account for part of the moisture differences between their plastic limits.

Diaspore

The plastic limits ranged from 20 for sodium diaspore to 26 for lithium diaspore, in the order: $Li \geqq Ca = K = NH_4 \geqq Mg \geqq Na$. There was only 3 percent moisture difference between lithium and magnesium diaspore, and only 3 percent difference between magnesium and sodium diaspore. In fact, the difference between the high and low values was so small that all the limits for diaspore can be considered equivalent except possibly that of sodium diaspore, which had the lowest plastic limit.

Gibbsite

The plastic limits ranged from 22 for ammonium gibbsite to 27 for magnesium gibbsite, in the order: $Mg \geqq Li = Na \geqq Ca = K \geqq NH_4$. As in the diaspores, the difference between the high and low plastic limits is so small that all the limits can probably be considered equivalent.

Liquid Limits

The liquid limits ranged from 27 percent moisture for sodium diaspore to 700 percent for sodium montmorillonite 3.

White (1949, p. 508) found that the liquid limits were: sodium montmorillonite > calcium montmorillonite > attapulgite > illite > kaolinite. Data from this investigation (table 2), which includes a greater number of clay minerals, indicate that lithium and sodium montmorillonites > attapulgite > calcium, magnesium, potassium, and ammonium montmorillonites > illites > kaolinite 1 > halloysite 2 ($4H_2O$) > halloysite 1 ($2H_2O$) > gibbsite > kaolinite 2 > diaspore.

Montmorillonite

The liquid limits of the montmorillonites (table 2) ranged from 108 for potassium montmorillonite 4 to 700 for sodium montmorillonite 3, in the order: montmorillonite 1, $Li > Na > NH_4 > Ca > K \geqq Mg$; montmorillonite 2, $Li > Na > Mg \geqq Ca \geqq K > NH_4$; montmorillonite 3, $Na > Li > NH_4 > K >$

Ca>Mg; and montmorillonite 4, Li>Na>NH_4≧Mg≧Ca>K.

Montmorillonite 3 had the widest range of liquid limits: 162 for magnesium to 700 for sodium. For montmorillonite 1, the liquid limit range was 158 for magnesium to 638 for lithium. For montmorillonite 2, the liquid limits ranged from 114 for NH_4 to 565 for lithium. For montmorillonite 4, which had the least spread between the high and low liquid limits, the values were between 108 for potassium and 292 for lithium. The liquid limit for lithium montmorillonite 1 was almost twice as great as that for sodium montmorillonite 1, and the liquid limit for lithium montmorillonite 2 was one-fourth higher than that for the sodium sample.

In contrast, for montmorillonite 3 the liquid limit of the sodium sample was higher by 100 units than that of the lithium sample. The data in table 2 show that lithium montmorillonites tended to give higher liquid limits than did the sodium samples, ammonium higher than potassium, and calcium and magnesium about the same. Most calcium and magnesium montmorillonites had liquid limits ranging around 175±25 percent moisture. The range for potassium and ammonium was 100 to 300; for sodium, 300 to 700; and for lithium, 600±100.

Sodium and lithium montmorillonites had the highest liquid limit values (lithium usually>sodium). All the other homoionic montmorillonites had much lower liquid limit values, on the order of one-fourth to one-third the values for sodium and lithium. Montmorillonite 4 differed from the other montmorillonites in that the liquid limits were generally lower; for sodium and lithium the values were generally half those of the other sodium and lithium montmorillonites.

When the clay-water mixtures were prepared for the various homoionic montmorillonites, one important difference was observed between sodium and lithium montmorillonites 2 and 3. Montmorillonite 3 sodium and lithium mixtures set into gels immediately, whereas montmorillonite 2 sodium and lithium mixtures took several days to gel. When stirred, the montmorillonite 3 mixture again set up into gels immediately, but sodium and lithium montmorillonites 2 again required several days to set up into gels.

Attapulgite

The liquid limits ranged from 158 percent moisture for ammonium attapulgite to 232 percent for calcium attapulgite, in the order: Ca>Li>Na>Mg>K>NH_4. Attapulgite is distinctive in that calcium gave much higher liquid limit values than did magnesium, and it differed from the montmorillonite in that calcium values were higher than those of the sodium and lithium samples.

Illite

The range between the highest and lowest liquid limits of the illites (from 59 for sodium illite 2 to 100 for calcium illite 3) was low compared with that of the montmorillonites and only about half as great as that of the attapulgites, indicating that the cation composition had relatively less influence. The orders for the various cations were: illite 1, Ca≧Mg≧NH_4≧K≧Li≧Na; illite 2, K≧Mg≧Ca≧Li≧NH_4≧Na; and illite 3, Ca≧Mg≧Li≧NH_4≧Na≧K.

For homoionic illites 1 the liquid limits ranged from 61 for sodium to 90 for calcium; for illites 2, from 59 for sodium to 72 for potassium; and for illites 3, from 72 for potassium to 100 for calcium.

An analysis of the data in table 2 suggests that the divalent cations give higher liquid limit values than do the monovalent cations (70 to 100 for calcium and magnesium, 60 to 85 for potassium and ammonium, and 60 to 90 for sodium and lithium).

The liquid limit values for sodium illites 1 and 2 were lower than those of the other cations, but the values for sodium and lithium illites 3 were equal to or greater than those for potassium and ammonium.

Kaolinite

The liquid limits ranged from 29 for sodium kaolinite 2 to 75 for ammonium kaolinite 1. For kaolinite 1, a poorly crystallized plastic kaolinite, the range was 52 for sodium to 75 for ammonium; and for kaolinite 2, a well crystallized kaolinite with little plasticity, the range was 29 for sodium to 39 for magnesium. The order was: kaolinite 1, $NH_4 \geqq Ca \geqq K \geqq Li \geqq Mg \geqq Na$; and kaolinite 2, $Mg \geqq Li \geqq K = NH_4 \geqq Ca \geqq Na$.

For kaolinite 2, sodium gave the lowest liquid limit value, but the difference between this value and those obtained for the other cations was so slight that it is probably of little significance. On the other hand, there is a possible significance to the greater variation between the value for sodium kaolinite 1 and the values for the other homoionic samples. Potassium and lithium gave equivalent liquid limit values for both kaolinites.

Halloysite

The liquid limits ranged from 36 for sodium halloysite 1 to 65 for calcium and magnesium halloysites 2. For the individual halloysites, the ranges were not so great. Thus, for halloysite 1 (halloysite $2H_2O$) the liquid limits ranged from 36 for sodium to 54 for calcium and magnesium; and for halloysite 2 (halloysite $4H_2O$), from 49 for lithium to 65 for calcium and magnesium. The orders for the various cations were: halloysite 1, $Ca = Mg > Li > NH_4 > K > Na$; and halloysite 2, $Ca = Mg > NH_4 > K > Na > Li$. For each clay, calcium and magnesium gave identical liquid limits which were higher than the values for the halloysites with monovalent cations. There was no systematic variation in values for the monovalent cations. Lithium gave equivalent liquid limits for both halloysites.

Diaspore

Diaspore had the lowest liquid limits of any of the clays studied. The values ranged from 27 for sodium to 42 for lithium, in the order: $Li > K > NH_4 > Ca = Mg > Na$.

Sodium diaspore had the lowest liquid limit, but the three other monovalent-cation diaspores (lithium, potassium, and ammonium) had higher liquid limits than did the divalent-cation diaspores studied.

Gibbsite

The liquid limits ranged from 33 for sodium gibbsite to 39 for magnesium gibbsite, in the order: $Mg = NH_4 \geqq Li \geqq K = Ca \geqq Na$. They can probably be considered almost equivalent, with sodium exhibiting the lowest value.

Plastic Index

The plastic index, also known as the plastic range, is the difference in percentage of moisture between the liquid and plastic limits. The plastic indices for the clays studied (table 3) ranged from 1 for sodium kaolinite 2 to 603 for sodium montmorillonite 3.

White (1949, p. 508) found that the plastic indices for a group of clay minerals were: montmorillonite $\geqq$ attapulgite $>$ illite $>$ kaolinite. Indications from the present study (table 3) are that montmorillonite $>$ attapulgite $>$ illite $>$ kaolinite 1 (poorly crystallized) $>$ gibbsite $>$ diaspore $=$ halloysite 1 ($2H_2O$) $=$ kaolinite 2 (well crystallized) $=$ halloysite 2 ($4H_2O$). Kaolinite 2, both halloysites, diaspore, and gibbsite have almost equivalent plastic indices.

Montmorillonite

The plastic indices ranged from 32 for potassium montmorillonite 4 to 603 for sodium montmorillonite 3, in the following orders for the various cations: montmorillonite 1, $Li > Na > NH_4 > K > Ca \geqq Mg$; montmorillonite 2, $Li > Na > Mg > Ca > K > NH_4$; montmorillonite 3, $Na > Li > NH_4 > K > Ca > Mg$; and montmorillonite 4, $Li > Na > NH_4 > Mg > Ca > K$.

For montmorillonite 1, the plastic indices ranged from 99 for magnesium to 558 for lithium; for montmorillonite 2, from 39 for ammonium to 506 for lithium; for montmorillonite 3, from 109 for magnesium to 603 for sodium; and for montmorillonite 4, from 32 for potassium to 210 for lithium.

Table 3.—Atterberg Plastic Indices

Clay Mineral	Adsorbed Cations					
	Ca^{++}	Mg^{++}	K^{+}	NH_4^{+}	Na^{+}	Li^{+}
Montmorillonite						
1	101	99	104	139	251	558
2	90	148	68	39	354	506
3	114	109	237	263	603	540
4	44	65	32	66	194	210
Attapulgite	108	70	57	61	112	123
Illite						
1	50	44	38	40	27	27
2	33	36	32	23	25	25
3	58	55	31	37	34	49
Kaolinite						
1	37	30	31	41	26	34
2	8	11	7	7	1	9
Halloysite						
1	16	7	4	11	7	12
2	7	5	2	5	2	2
Diaspore	7	8	9	8	7	16
Gibbsite	11	12	11	17	7	12

Lithium montmorillonite 1 had a plastic index about 2.2 times greater than that of sodium montmorillonite 1, and lithium montmorillonite 2 had a plastic index 1.4 times higher than that of sodium. However, for montmorillonite 3, sodium gave a plastic index 1.1 times higher than did lithium; and for montmorillonite 4, the plastic index for lithium was 17 units higher than that for sodium.

Sodium and lithium gave the highest plastic indices, but in a given clay either one could be higher. All other cations gave much lower plastic indices. The indices for most lithium montmorillonites are probably 525 ± 35 units; for sodium, 400 ± 200; for potassium, 125 ± 100; for ammonium, 150 ± 125; for magnesium, 125 ± 25; and for calcium, 100 ± 25.

Ammonium montmorillonites tended to have higher plastic indices than did the potassium montmorillonites. Montmorillonite 3, which is the natural high-swelling montmorillonite, had much higher plastic indices for ammonium and potassium than did the montmorillonites that do not swell appreciably in the natural state.

In comparing samples with the same cations, montmorillonite 4, which has a low cation exchange capacity, was found to have much lower plastic indices than the other montmorillonites.

Attapulgite

The plastic indices ranged from 57 for potassium attapulgite to 123 for lithium attapulgite, in the order: $Li>Na>Ca>Mg>NH_4>K$. Lithium, sodium, and calcium gave indices of more than 100; and magnesium, ammonium, and potassium gave indices between 55 and 70, indicating that the sodium, lithium, and calcium attapulgites have a wider plastic range than do the magnesium, potassium, and ammonium attapulgites.

Illite

The plastic indices ranged from 23 for ammonium illite 2 to 58 for calcium illite 3. Homoionic illites 1 and 3 had a wider range of plastic indices than did homoionic

illites 2. For illites 1, the range was from 27 for sodium and lithium to 50 for calcium; for illites 2, from 23 for ammonium to 36 for magnesium; and for illites 3, from 31 for potassium to 58 for calcium. The orders for the various cations were: illite 1, $Ca > Mg > NH_4 \geqq K > Na = Li$; illite 2, $Mg \geqq Ca \geqq K > Na = Li \geqq NH_4$; and illite 3, $Ca \geqq Mg > Li > NH_4 \geqq Na \geqq K$.

The divalent cations produced higher plastic indices than did the monovalent cations. There appeared to be no regularity among the monovalent cations in the plastic indices they produced and no significant difference between the values they yielded.

Kaolinite

The plastic indices ranged from 1 for sodium kaolinite 2 to 41 for ammonium kaolinite 1. The orders for the various cations were: kaolinite 1, $NH_4 > Ca \geqq Li \geqq K \geqq Mg > Na$; kaolinite 2, $Mg \geqq Li \geqq Ca \geqq NH_4 = K > Na$.

For kaolinite 2, the well crystallized kaolinite, the plastic indices ranged from 1 for sodium to 11 for magnesium; and for kaolinite 1, the poorly crystallized kaolinite, from 26 for sodium to 41 for ammonium. When comparing respective cations, the indices for kaolinite 1 are from 2½ to 26 times greater than for kaolinite 2. Sodium gave the lowest plastic index for each kaolinite. There appeared to be no fixed relationship for the other cations.

Halloysite

The plastic indices ranged from 7 for sodium and lithium halloysites 2 to 16 for calcium halloysite 1. The orders for the various cations were: halloysite 1, $Ca > Li > NH_4 \geqq Mg = Na > K$; halloysite 2, $Ca \geqq Mg = NH_4 \geqq Li = K = Na$. The indices for halloysite 1 ranged from 4 for potassium to 16 for calcium; and for halloysite 2, from 2 for sodium, lithium, and potassium to 7 for calcium.

Potassium gave the lowest indices for both halloysites, and calcium the highest. From the data in tables 1 and 2, it can be seen that the plastic and liquid limits were higher for halloysites 2 ($4H_2O$) than for halloysites 1 ($2H_2O$). Table 3 also shows that halloysites 1 had a wider plastic range than halloysites 2.

Diaspore

The plastic indices ranged from 7 for sodium and calcium diaspore to 16 for lithium. The order for the various cations was: $Li > K \geqq NH_4 \geqq Mg = Ca = Na$.

Gibbsite

The plastic indices ranged from 7 for sodium gibbsite to 17 for ammonium. The order for the various cations was: $NH_4 > Mg = Li > K = Ca > Na$.

Slope of the Liquid Limit Line

Slopes of the liquid limit lines are presented in table 4. The angles of slope range from about 3° for sodium gibbsite to almost 74° for lithium montmorillonite 3. Three clays (ammonium, sodium, and lithium montmorillonites 3) have slopes between 70° and 75°. Only six clays have slopes greater than 45°: ammonium, sodium, and lithium montmorillonites 3; sodium and lithium montmorillonites 2; and lithium montmorillonite 4. Only ten montmorillonite clays have slopes greater than 35°: the sodium and lithium montmorillonites, ammonium montmorillonite 3, and calcium montmorillonite 1.

All other clay minerals give smaller angles—generally much smaller. The data suggest that there are only fifteen clays with slopes over 20° and only twenty-five clays (less than a third) with slopes greater than 15°. Almost half the clays have slopes less than 10°.

Montmorillonite

The angles of slope for the homoionic montmorillonites ranged from 4° for calcium montmorillonite 4 to 74° for lithium montmorillonite 3. Three samples, sodium, ammonium, and lithium montmorillonite 3, have slopes between 70° and 75°. Only three other samples have slopes greater than 45°: sodium and lithium montmorillonite 2 and lithium montmorillonite 4. Four others have slopes greater than 35°:

TABLE 4.—ANGLE OF SLOPE OF LIQUID LIMIT LINE, IN DEGREES

Clay Mineral	Adsorbed Cations					
	Ca^{++}	Mg^{++}	K^{+}	NH_4^{+}	Na^{+}	Li^{+}
Montmorillonite						
1	39	17	17	13	35	37
2	20	32	5	9	59	59
3	26	23	19	70	73	74
4	4	11	6	8	44	48
Attapulgite	34	27	5	27	14	29
Illite						
1	14	13	11	11	4	7
2	25	15	13	6	12	9
3	16	18	6	9	5	13
Kaolinite						
1	13	16	11	12	7	16
2	7	11	7	5	7	10
Halloysite						
1	8	4	12	6	5	7
2	8	7	3	5	3	6
Diaspore	6	12	9	8	5	14
Gibbsite	5	10	5	6	3	6

sodium, lithium, and calcium montmorillonite 1 and sodium montmorillonite 4.

The slopes for the homoionic samples of each montmorillonite are as follows: montmorillonite 1, $Ca>Li>Na>Mg=K>NH_4$; montmorillonite 2, $Li=Na>Mg>Ca>NH_4>K$; montmorillonite 3, $Li>Na>NH_4>Ca>Mg>K$; montmorillonite 4, $Li>Na>Mg>NH_4>K>Ca$.

Lithium and sodium montmorillonites tend to have angles of slope greater than 35°; potassium and ammonium montmorillonites, less than 20°; and calcium and magnesium montmorillonites, between 20° and 40°.

Attapulgite

For the attapulgites the slopes range from 5° for potassium to 34° for calcium, in the order: $Ca>Li>Mg=NH_4>Na>K$.

Illite

For the illites the angle of slope varies from 4° to 25°, in the following orders: illite 1, $Ca>Mg>NH_4=K>Li>Na$; illite 2, $Ca>Mg>K>Na>Li>NH_4$; and illite 3, $Mg>Ca>Li>NH_4>K>Na$. The divalent-cation illites have greater angles of slope than do the monovalent ones: from 10° to 25° for the divalent, and from about 5° to 15° for the monovalent.

There is only one illite with an angle of slope greater than 20°, calcium illite 2; and there are only two with angles of slope between 15° and 20°, calcium and magnesium illite 3. Eight illites have slopes between 10° and 15°, and five have slopes between 5° and 10°. Sodium illite 1 and sodium illite 3 have slopes less than 5°.

Kaolinite

The angles of slope for kaolinite range from 5° for ammonium kaolinite 2 to 16° for lithium and magnesium kaolinite 1. Kaolinite 1, the poorly crystallized kaolinite, has greater angles of slope than does kaolinite 2, the well crystallized kaolinite. The angles of slope for kaolinite 1 range from 7° for sodium to 16° for lithium and magnesium; and for kaolinite 2, they vary from 5° for ammonium to almost 11° for magnesium. For kaolinite 1 the angles of

slope have the following orders: Li>Mg>Ca>NH_4>K>Na; for kaolinite 2, Mg>Li>Ca=K>Na>NH_4.

For kaolinite 1 most of the slopes tend to be greater than 10°, but for kaolinite 2 most of the slopes tend to be between 5° and 10°. Sodium tends to give low angles of slope, whereas lithium and magnesium tend to give greater angles of slope.

Halloysite

The angles of slope for the halloysites range from 3° for potassium and sodium halloysites 2 to 12° for potassium halloysite 1. The angles of slope for the various cations are: halloysite 1, K>Ca>Li>NH_4>Na>Mg; halloysite 2, Ca>Mg>Li>NH_4>K>Na.

For halloysite 1 the slopes range from 4° for magnesium to about 12° for potassium; and for halloysite 2 they range from 3° for potassium and sodium to about 8° for calcium. The halloysites 1 have greater angles of slope than do the halloysites 2, although the halloysites 2 have higher plastic and liquid limits.

Only one halloysite has slopes above 10°, but four halloysites have slopes less than 5°. For halloysite 2, half the slopes are above 5°, and half are below 5°.

Diaspore

For diaspore, the range is from 5° for sodium to 14° for lithium, in the order: Li>Mg>K>NH_4>Ca>Na. Two diaspores have slopes greater than 10°, and the other four have slopes between 5° and 10°.

Gibbsite

For gibbsite, the range is from 3° for sodium to 10° for magnesium, in the order: Mg>Li=NH_4>K=Ca>Na.

Water Sorption

The sorption curves are plotted as semilogarithmic graphs: time along the logarithmic (abscissa) scale and adsorbed moisture along the arithmetic (ordinate) scale. A straight line indicates that the average sorption rate is equal to one-half the sorption rate of the time interval preceding it and twice the average sorption rate of the time interval following it. If a curve turns toward the vertical, either the average sorption rate has increased or the sorption rate did not decrease to half the average sorption rate of the preceding time interval. If a curve turns toward the horizontal, the average rate of sorption is less than half the average rate of the preceding time interval.

For descriptive purposes, normal sorption rate is here considered as that decrease in rate that will give a straight line with one scale logarithmic and the other scale arithmetic. Sorption rates which cause the curves to turn toward the vertical (ordinate) are considered above normal, and sorption rates which cause the curve to turn toward the horizontal (abscissa) are considered below normal.

Montmorillonite

The sorption curves for the homoionic montmorillonites 1 (fig. 3) indicate that all of them took up water slowly for the first two minutes, after which the rates differed. Water sorption for the calcium montmorillonite was the most rapid and was virtually complete in 30 minutes, about 200 percent water having been adsorbed. The rate of sorption for the lithium montmorillonite was the next most rapid and continued at a high rate to about 3600 minutes, at which time the clay mineral had taken up about 650 percent water.

The sodium montmorillonite adsorbed water very slowly for the first 10 minutes. It then increased above normal and was continuing to swell at 7200 minutes when it had taken up 540 percent water. Magnesium, ammonium, and potassium montmorillonites 1 took up water initially at about the same rate as did the sodium montmorillonite: 200 percent water in 900 minutes for magnesium, 350 percent in 3600 minutes for ammonium, and 275 percent in 3600 minutes for potassium. The order of water sorption for the various cations was: Li>Na>NH_4>K>Ca>Mg.

The curves for the homoionic montmorillonites 2 (fig. 4) indicate that up to two minutes the calcium, magnesium, and so-

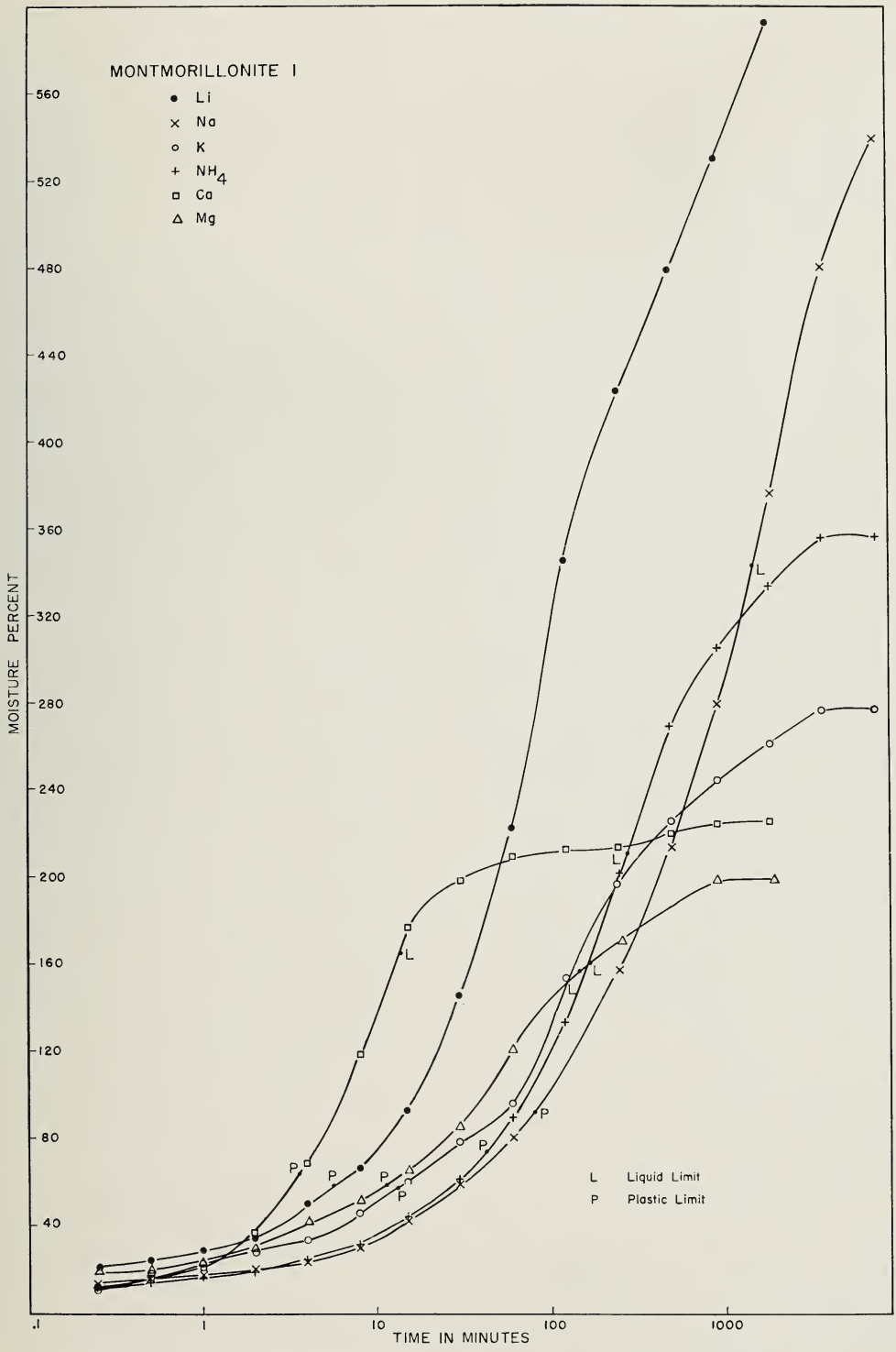

FIG. 3.—Water sorption curve for homoionic montmorillonite 1.

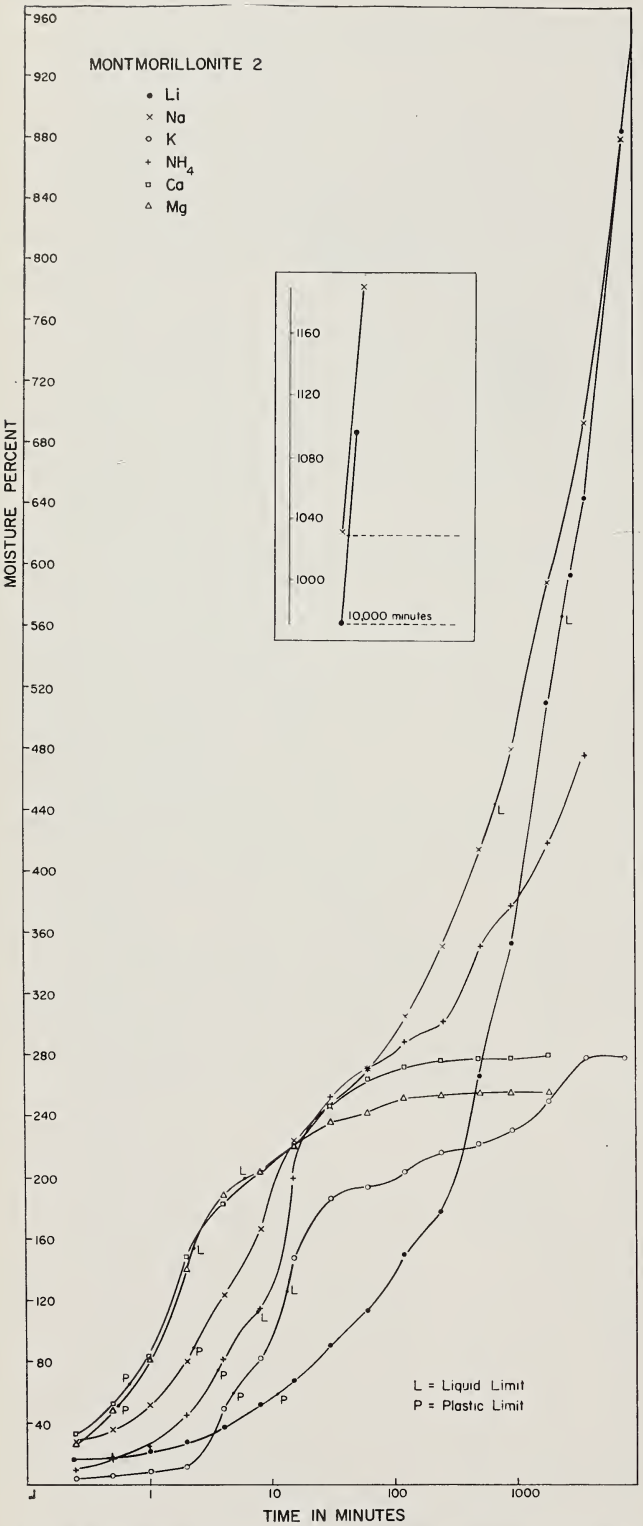

Fig. 4.—Water sorption curve for homoionic montmorillonite 2.

dium montmorillonites adsorbed water more rapidly than did the other montmorillonites 2. The curves for magnesium and calcium show the same sorption rates for the first 20 minutes and then diverge; water sorption was virtually complete at the end of 100 minutes, when the clay minerals had adsorbed 250 and 270 percent water, respectively.

Lithium montmorillonites 2 and 1 had about the same water sorption rates up to about 3600 minutes, at which time sorption for lithium montmorillonite 1 was complete. Lithium montmorillonite 2 continued sorption, adsorbing 1100 percent water in 14,400 minutes, at which time there was still no indication of a diminution of normal sorption rate. Sodium montmorillonite 2 had a much more rapid rate of sorption than did sodium montmorillonite 1, adsorbing 1190 percent water in 14,400 minutes, with the curve suggesting that sorption was not complete.

Ammonium montmorillonite 2 began sorption much more slowly than did sodium montmorillonite 2, but after one minute sorption took place at a more rapid rate until, at the end of 30 minutes, both montmorillonites had adsorbed about the same amount of water. However, after 30 minutes the water sorption rate for ammonium became slower, and the two curves began to diverge. In 1800 minutes the ammonium montmorillonite 2 had adsorbed 480 percent water, but the curve indicates that sorption would continue if more time were permitted. The rate of water sorption for potassium montmorillonite 2, 280 percent water in 3600 minutes, was about the same as that for potassium montmorillonite 1. The order of maximum water sorption for the various cations was: $Na > Li > NH_4 > Ca \geqq K > Mg$.

The curves for the homoionic montmorillonites 3 (fig. 5) indicate that all the samples adsorbed water slowly for the first two minutes, after which lithium began to adsorb water very rapidly and adsorbed 780 percent water in 14,400 minutes. The curve suggests that it was still adsorbing water at the end of that time.

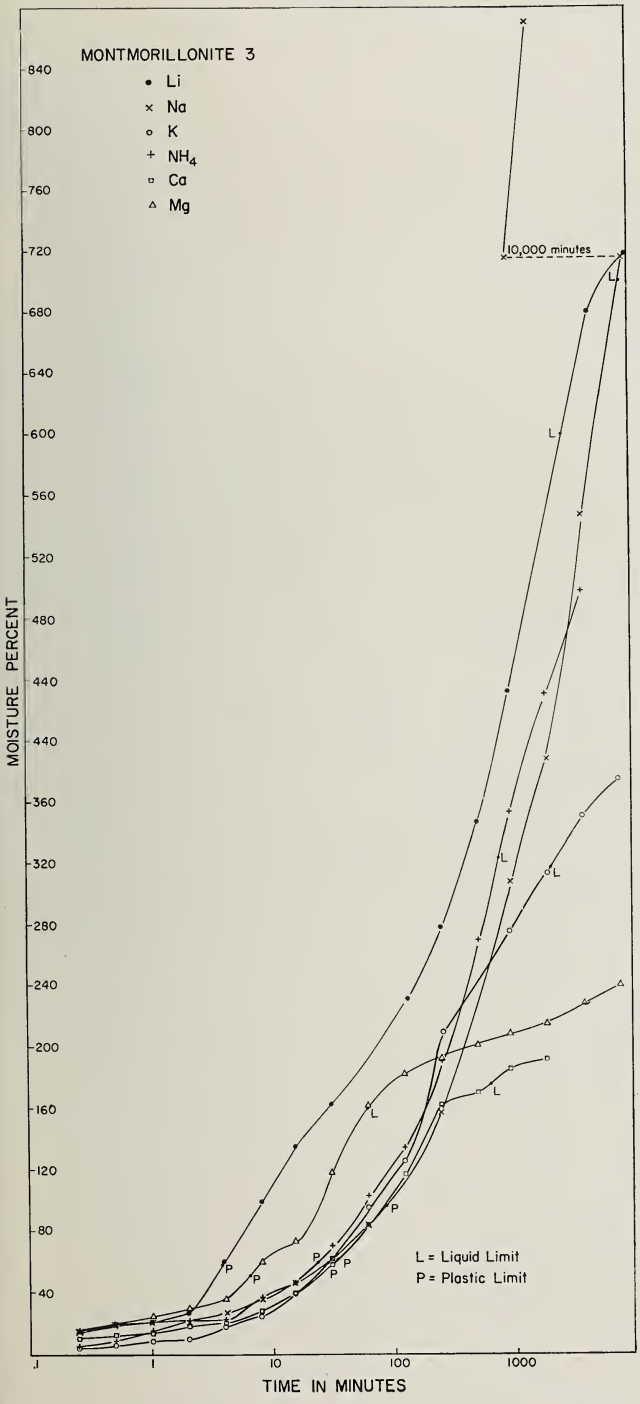

Fig. 5.—Water sorption curve for homoionic montmorillonite 3.

Calcium, sodium, ammonium, and potassium adsorbed water slowly for the first 10 minutes then much more rapidly up to 240 minutes and 165 percent water, after which time calcium adsorbed little more water. The three monovalent-cation clay minerals continued sorption at about equal rates up to 480 minutes, at which point the rate for potassium decreased slightly; however, at 1800 minutes it had adsorbed 375 percent water and was still adsorbing at a rapid rate. The rate for ammonium began to diminish after 900 minutes when it had adsorbed 360 percent water; at 3600 minutes it had adsorbed about 500 percent. Sodium had adsorbed 870 percent in 14,400 minutes, and the curve suggests that it was still continuing to adsorb. Magnesium, after four minutes of slow water sorption, formed a new normal with a much more rapid sorption rate, but after 60 minutes the rate began to decrease. In 900 minutes the magnesium montmorillonite had taken up about 210 percent moisture. The order of water sorption with the various cations was: $Na > Li > NH_4 > K > Mg > Ca$.

The homoionic montmorillonites 4 (fig. 6) differed from the other homoionic montmorillonites in that initial water sorption was rapid: for all but the sodium and lithium montmorillonites 4, water sorption was well on its way to completion in 1 minute. Water sorption for sodium montmorillonite 4 was rapid up to two minutes and 280 percent water but the rate gradually diminished as sorption continued up to 480 percent water at 3600 minutes, at which time sorption was essentially complete.

Lithium took up water very rapidly for the first 15 seconds, adsorbing 35 percent water. Sorption was then slow for one minute but the rate gradually increased above normal until it was complete at 3600 minutes and 355 percent water.

Calcium montmorillonite 4 adsorbed 160 percent water in the first 15 seconds and 65 percent more in the next 1800 minutes, at which time sorption was complete. Ammonium montmorillonite 4 took up 130 percent water in the first 30 seconds and 95

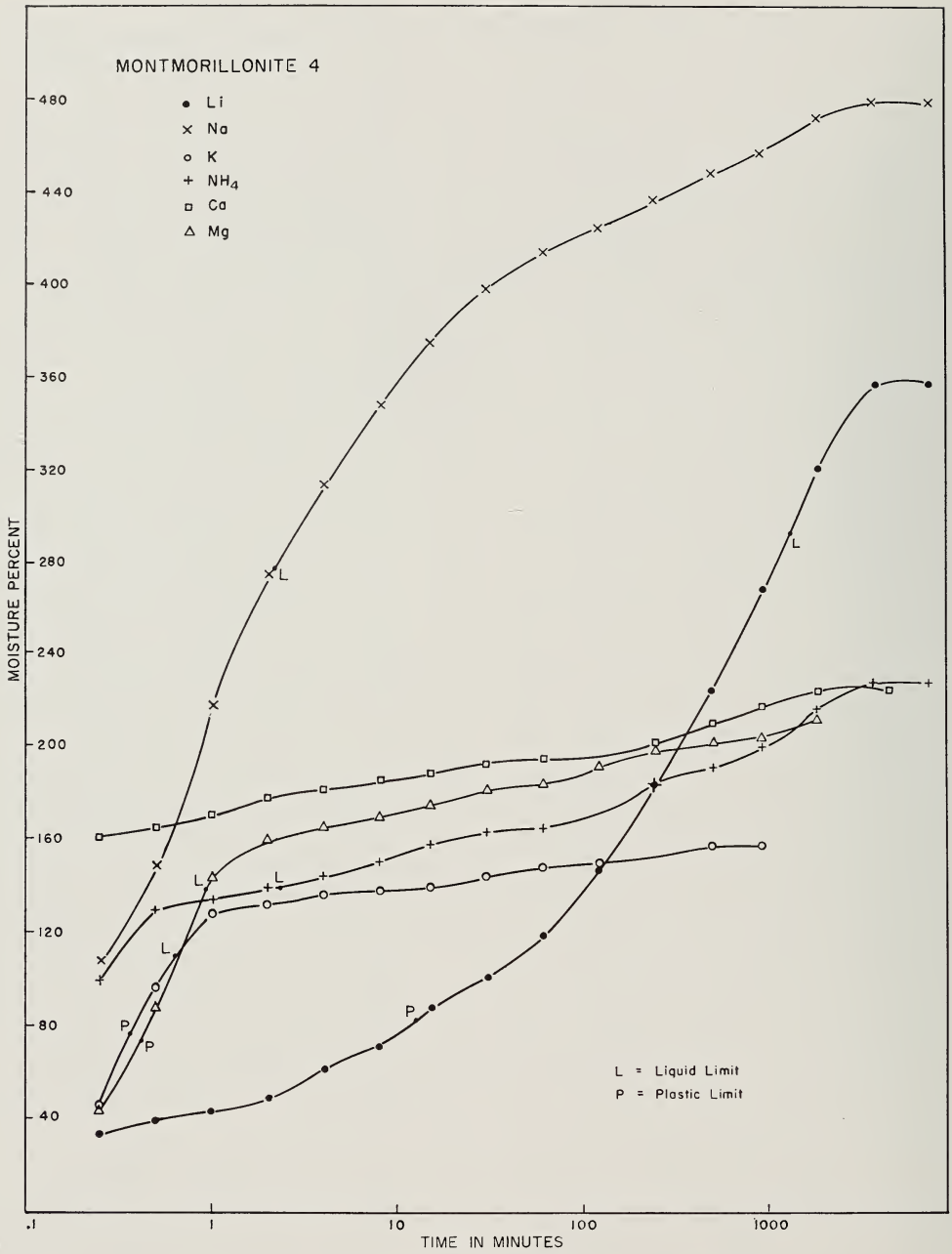

Fig. 6.—Water sorption curve for homoionic montmorillonite 4.

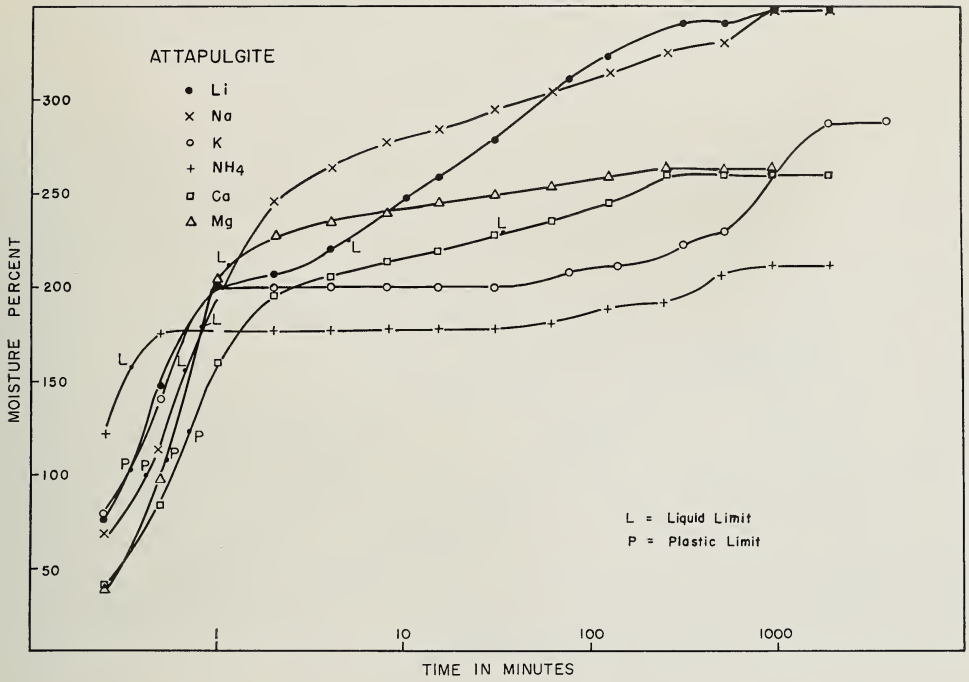

FIG. 7.—Water sorption curve for attapulgite.

percent more in the next 3600 minutes, sorption then being complete.

Magnesium montmorillonite 4 took up 145 percent water in the first minute and 60 percent more in the next 900 minutes, at which time sorption was essentially complete. The order of sorption with the various cations was: $Na > Li > Ca > Mg > NH_4 > K$.

In summary, most of the montmorillonites took up little water in the first two minutes, although some, notably the montmorillonites 4, started adsorbing water rapidly. After this the curves show a great divergence.

There appears to be no relationship between cation and rate of adsorption, but there is a relationship between cation and amount of adsorption. The lithium and sodium montmorillonites adsorbed the greatest amount of water regardless of whether sorption rate was fast or slow. The ammonium montmorillonites tended to adsorb more water than did the potassium, calcium, and magnesium ones but less than the sodium and lithium ones.

Water sorption for the calcium, magnesium, and potassium montmorillonites was generally much less than for the other homoionic montmorillonites. After a slow initial start, they adsorbed water rapidly to about 100 minutes with about 200 percent water, after which time little further sorption took place.

Attapulgite

All attapulgites, regardless of adsorbed cations, took more than half their water of sorption in the first minute. After the first minute the rate of sorption was reduced, as indicated by the curves in figure 7.

Sodium attapulgite took up 200 percent water in one minute, after which the rate diminished; however, sorption continued to 900 minutes and 350 percent water, at which time sorption was complete. For lithium attapulgite the reduction in rate of sorption began at one minute and about

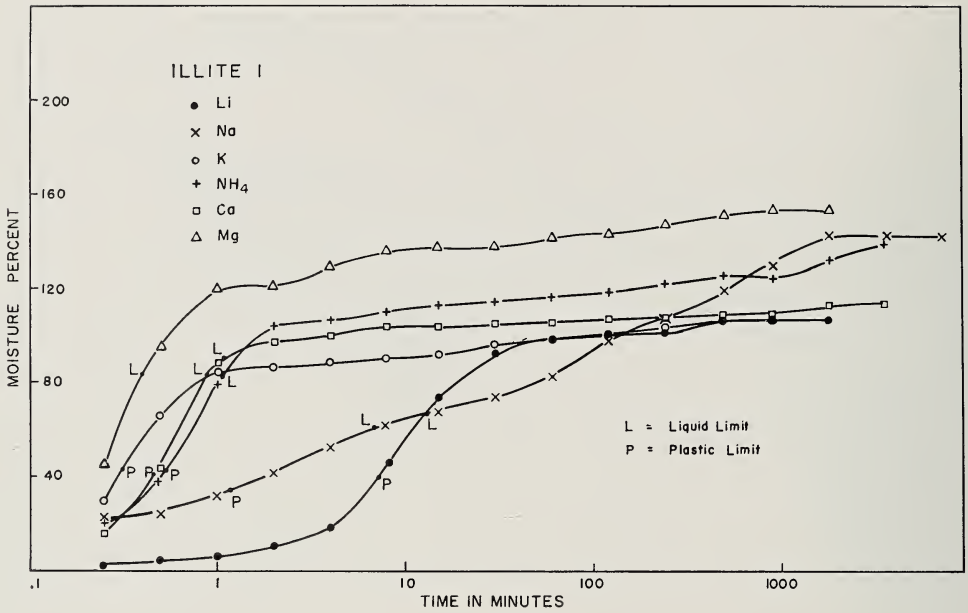

Fig. 8.—Water sorption curve for illite 1.

170 percent moisture but the normal rate was only slightly reduced, and sorption continued up to completion in 900 minutes and 350 percent water.

Ammonium attapulgite adsorbed 176 percent water in 30 seconds, underwent a complete hiatus for eight minutes, began water sorption again very slowly, and then increased the normal rate to 450 minutes and 212 percent water. Potassium attapulgite adsorbed 200 percent water in the first minute, had a hiatus to 30 minutes, began water sorption again and continued to 800 minutes and 290 percent water, when sorption was complete.

Calcium attapulgite took up water very rapidly for the first two minutes, at which time it had adsorbed 196 percent water. After two minutes the rate diminished, although sorption continued to completion at 240 minutes and 260 percent water. Magnesium attapulgite took up 205 percent water in one minute and then the rate diminished. Water sorption was complete in 480 minutes and 265 percent water. The order of maximum sorption with the various cations was: $Na=Li>K>Mg>Ca=NH_4$.

Illite

The curves for the illites 1 (fig. 8) indicate that the initial sorption rate was rapid except for the lithium sample. Magnesium illite 1 adsorbed 120 percent water in the first minute but only 34 percent more water in the next 900 minutes, at which time sorption was complete. Potassium illite 1 adsorbed 84 percent water in the first minute but only 24 percent more water in the next 480 minutes, at which time sorption was complete.

Calcium illite 1 adsorbed 97 percent water in the first two minutes but only 11 percent water in the next 900 minutes, at which time sorption was complete. Ammonium illite 1 adsorbed 104 percent water in the first two minutes, but only 35 percent more water in the next 3600 minutes. The curve suggests that sorption was not yet complete.

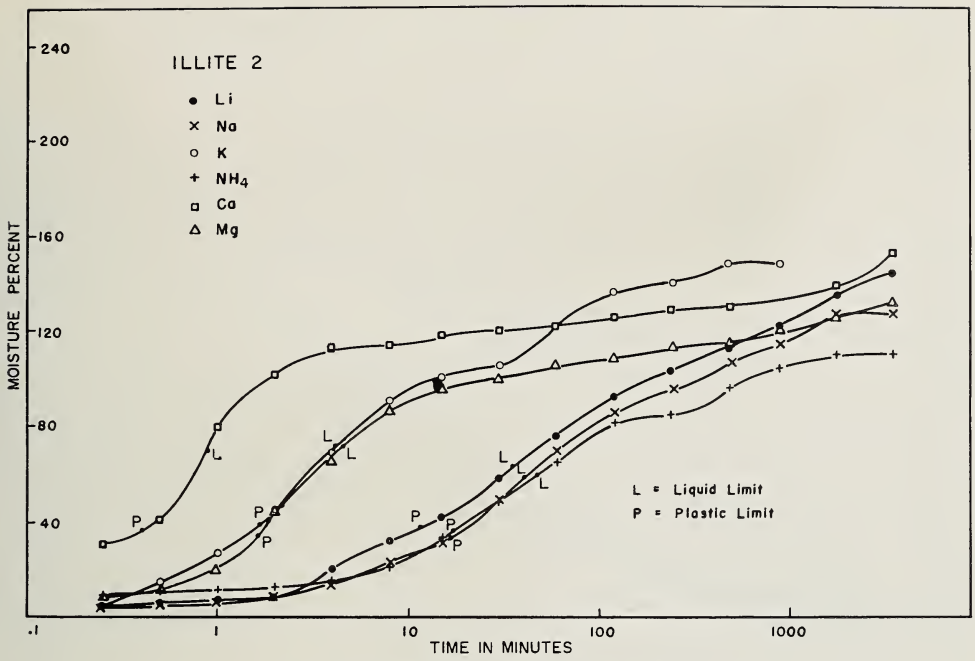

Fig. 9.—Water sorption curve for illite 2.

Sodium illite 1 adsorbed 26 percent water in the first 15 seconds but only 142 percent in the next 1800 minutes, at which time sorption was complete. Lithium illite 1 started water sorption slowly, adsorbing only 18 percent water in the first four minutes. From four to 60 minutes it adsorbed 80 percent water, and from 60 to 480 minutes it adsorbed 10 percent water, at which time sorption was complete. The order of maximum water sorption with the various cations was: $Mg > Na > NH_4 > Ca > Li > K$.

The curves for the illites 2 (fig. 9) indicate that, in contrast to the illites 1, the initial sorption rates for the various homoionic samples were slow at first, except for the calcium sample. Calcium illite 2 adsorbed 102 percent water in the first two minutes and 50 percent more water in the next 1800 minutes. The curve indicates that sorption was still continuing at this time. Potassium illite 2 adsorbed 27 percent water in the first minute and 148 percent in the next 480 minutes, at which time sorption was complete. Magnesium illite 2 adsorbed 20 percent water in the first minute and 68 percent more in the next seven minutes. From seven to 3600 minutes it adsorbed 44 percent more water, and sorption was not yet complete.

Ammonium illite 2 adsorbed 10 percent water in the first two minutes and 100 percent more water in the next 1800 minutes, at which time sorption was complete. Lithium and sodium illites 2 adsorbed 8 percent water in the first two minutes. In the next 1800 minutes the lithium illite adsorbed 128 percent more water and the sodium illite adsorbed 118 percent more water. Sorption for the lithium illite was not yet complete at the end of this time but was complete for the sodium illite. The order of maximum water sorption with the various cations was: $Ca > K > Mg > Li > Na > NH_4$.

The curves for the illites 3 (fig. 10) indicate that the initial sorption rate was rapid for calcium illite 3, intermediate for magnesium illite 3, and slow for the illites 3 with monovalent ions. Calcium illite 3 ad-

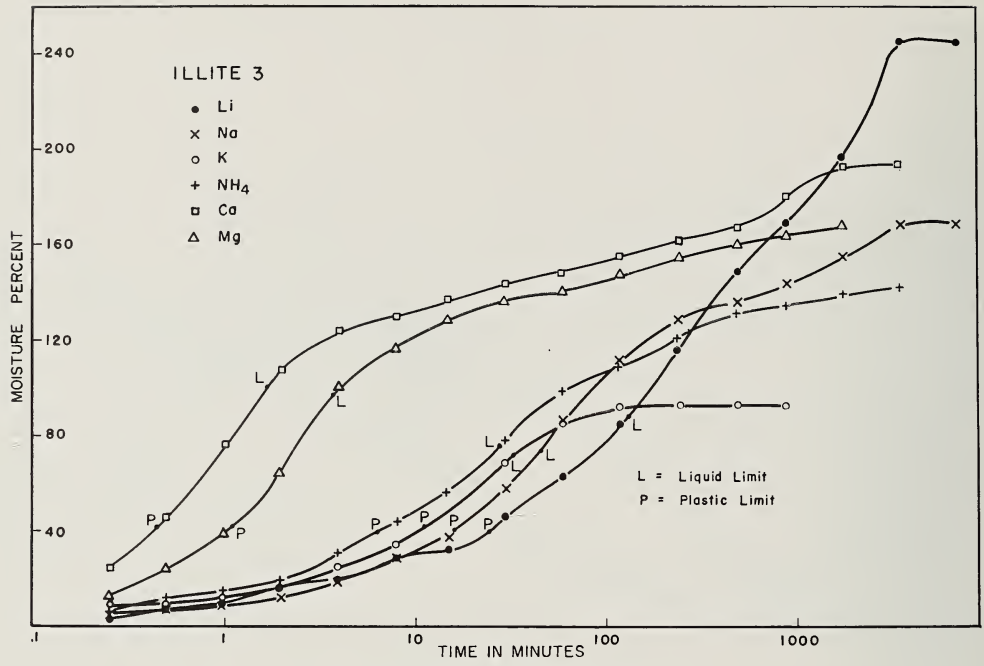

Fig. 10.—Water sorption curve for illite 3.

sorbed 124 percent water in four minutes and an additional 76 percent water in the next 1800 minutes, at which time sorption was complete. Magnesium illite 3 adsorbed 100 percent water in 4 minutes and an additional 78 percent water in the next 1800 minutes. The curve suggests possible continued sorption.

Ammonium illite 3 adsorbed 19 percent water in the first two minutes, at which time the rate increased, and 99 percent more water in the next 58 minutes. Then sorption continued more slowly, 43 percent more water being adsorbed in the next 50 minutes, with an indication that sorption might continue. Potassium illite 3 adsorbed 17 percent water in the first two minutes. The sorption rate gradually increased to 120 minutes, during which time the sample adsorbed 75 percent more water and completed sorption. Sodium illite 3 adsorbed 12 percent moisture in the first two minutes and increased the sorption rate gradually to 120 minutes, at which time the sample had adsorbed 98 percent more water. In the next 1680 minutes the sample adsorbed 45 percent more water, and there was an indication of continued sorption beyond this point. The order of maximum water sorption with the various cations was: $Li > Ca > Mg > Na > NH_4 > K$.

In summary, the sorption rates for the calcium illites were rapid for the first two minutes, at which time sorption was virtually complete. Sorption for the magnesium illites was almost complete in from one to 10 minutes and might be more or less rapid than for the calcium illites. Sorption by the lithium and sodium illites started slowly with little sorption in the first two to four minutes but after this the normal rate increased gradually. For the potassium and ammonium illites, sorption might begin rapidly and be nearly complete in one to two minutes, or it might begin slowly and continue slowly with only slight deviations from the normal until sorption was complete. There is no fixed relationship between the cations and order of maximum water sorption when the three illites are compared.

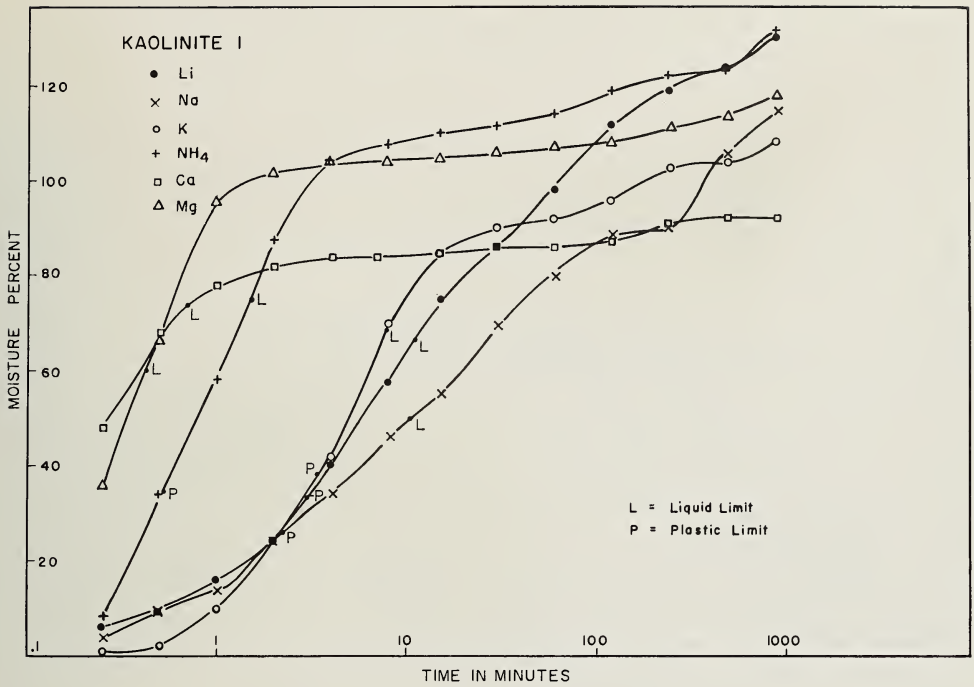

FIG. 11.—Water sorption curve for kaolinite 1.

Kaolinite

For the homoionic kaolinites 1 (fig. 11) the range of maximum water sorption was 92 percent for calcium to 129 percent for lithium, the order with the various cations being: $Li > NH_4 > Mg > Na > K > Ca$, with water sorption values of 129, 124, 118, 115, 103, and 92 percent, respectively.

Water sorption was most rapid in the case of calcium kaolinite 1, which took up most of the water in the first minute. Magnesium kaolinite 1 took up most of the water in the first two minutes, and ammonium kaolinite 1 did it in four minutes. On the other hand, sodium and lithium kaolinites 1 took up water slowly, adsorption proceeding at approximately the same rate for both during the first two minutes, after which sodium maintained an approximately normal adsorption rate and lithium adsorbed water more rapidly. Potassium kaolinite 1 took up water very slowly for the first half minute but then adsorbed much more rapidly than did either the sodium or lithium sample.

For the homoionic kaolinites 2 (fig. 12), the range of water sorption was less than for the homoionic kaolinites 1. The order with the various cations was: $NH_4 > Ca > Li > Mg = Na > K$, with maximum water sorption values of 80, 69, 54, 52, 52, and 48 percent. Calcium kaolinite 2 took up water most rapidly at the start but was soon overtaken by both ammonium and magnesium kaolinites 2. The magnesium sample had virtually completed water sorption in four minutes and the ammonium sample in eight minutes, but the calcium sample required 480 minutes for completion. Water sorption of the magnesium kaolinite was slow for the first half minute and that of the sodium, potassium, and lithium kaolinites, for the first minute. Sodium and lithium had completed water sorption in 15 minutes, whereas potassium required 120 minutes to complete sorption.

Halloysite

For the homoionic halloysites 1 (fig. 13), with the exception of sodium and magne-

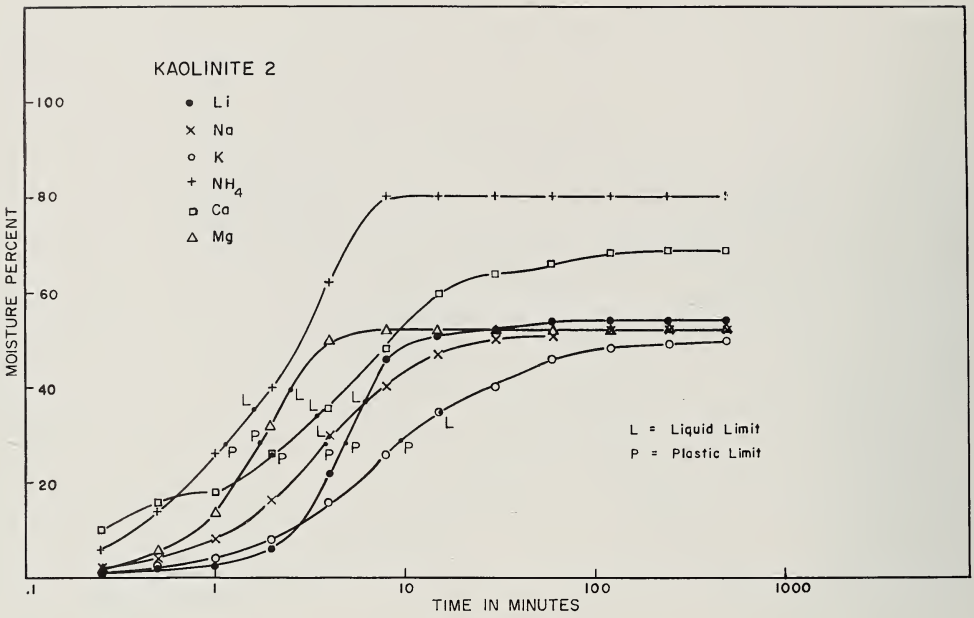

Fig. 12.—Water sorption curve for kaolinite 2.

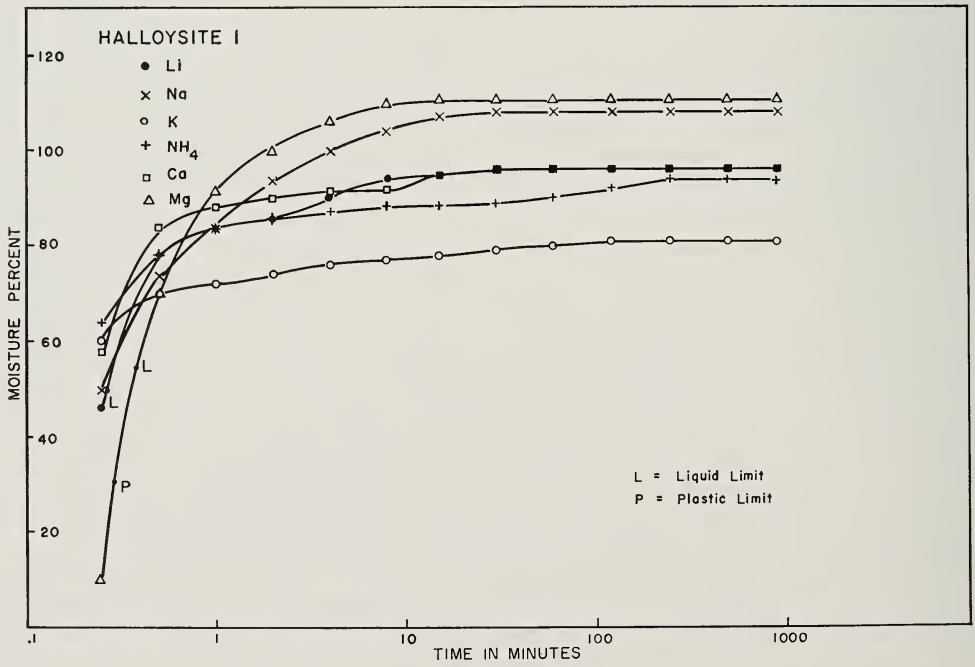

Fig. 13.—Water sorption curve for halloysite 1.

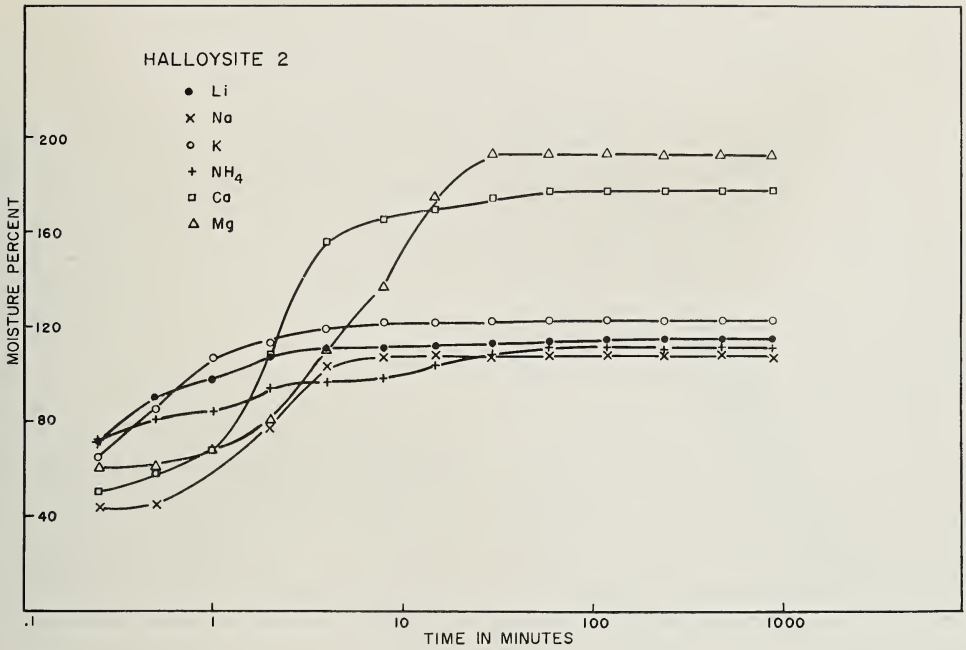

FIG. 14.—Water sorption curve for halloysite 2.

sium, water sorption was virtually completed in half a minute. The magnesium halloysite completed water sorption in 15 minutes and the sodium halloysite in 30 minutes. The order with the various cations was: $Mg>Na>NH_4>Ca=Li>K$, with maximum water sorption values of 111, 108, 97, 96, 96, and 81 percent.

Ammonium and potassium halloysites 1, although they had the most rapid initial sorption rate, took up the least water; magnesium, with the slowest sorption rate, took up the most water.

The homoionic halloysites 2 (fig. 14) took up more water than did the homoionic halloysites 1. As is generally true for halloysites 1, the initial water sorption was quite rapid; and, like magnesium halloysite 1, magnesium halloysite 2 took up the most water. The water sorption range for the homoionic halloysites 2 was: $Mg>Ca>K>Li>NH_4>Na$, with maximum values of 192, 176, 121, 114, 110, and 107 percent. Most of the water sorption took place in the first 15 minutes.

All the water sorption curves for the halloysites 2, except those for potassium and lithium, show a plateau after the first 15 seconds of water sorption, indicating a great reduction in rate of sorption. A minute or two later, sorption increased above the new normal. There are no plateaus in the water sorption curves for the halloysites 1.

Diaspore

Water sorption started much slower for the homoionic diaspores (fig. 15) than for the homoionic halloysites. There was little difference among the cations in the initial sorption rates. The order with the various cations was: $K=Na>Mg=NH_4>Ca>Li$, with maximum values of 58, 58, 53, 53, 52, and 47 percent.

Gibbsite

Water sorption by some of the homoionic gibbsites (fig. 16) was more rapid than by the homoionic diaspores. The order with the various cations was: $K>Na>Mg>NH_4>Ca>Li$, with maximum values of 88, 82, 81, 74, 72, and 71 percent. Magnesium and

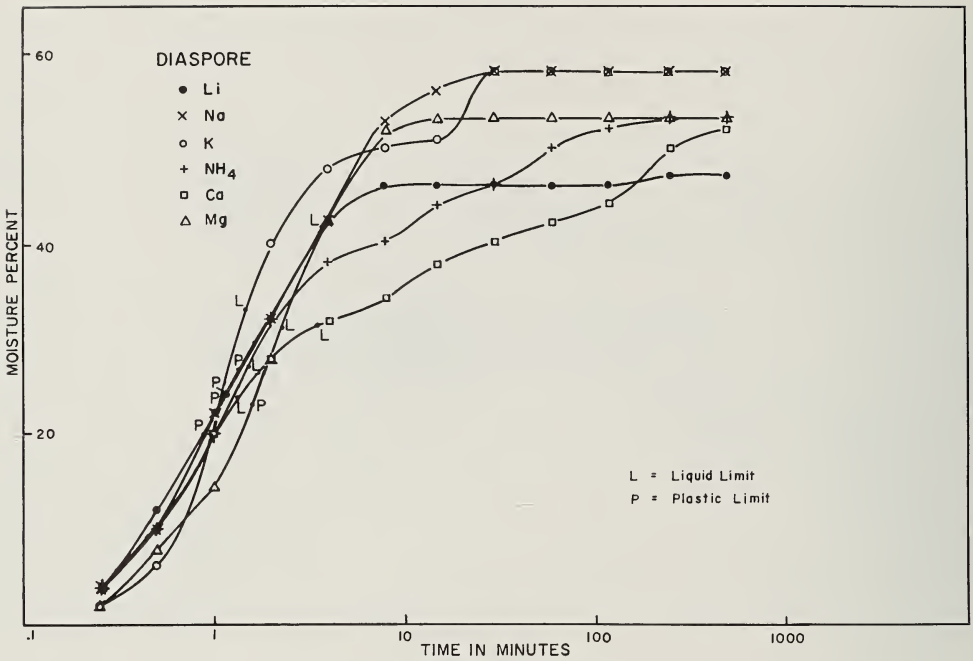

Fig. 15.—Water sorption curve for diaspore.

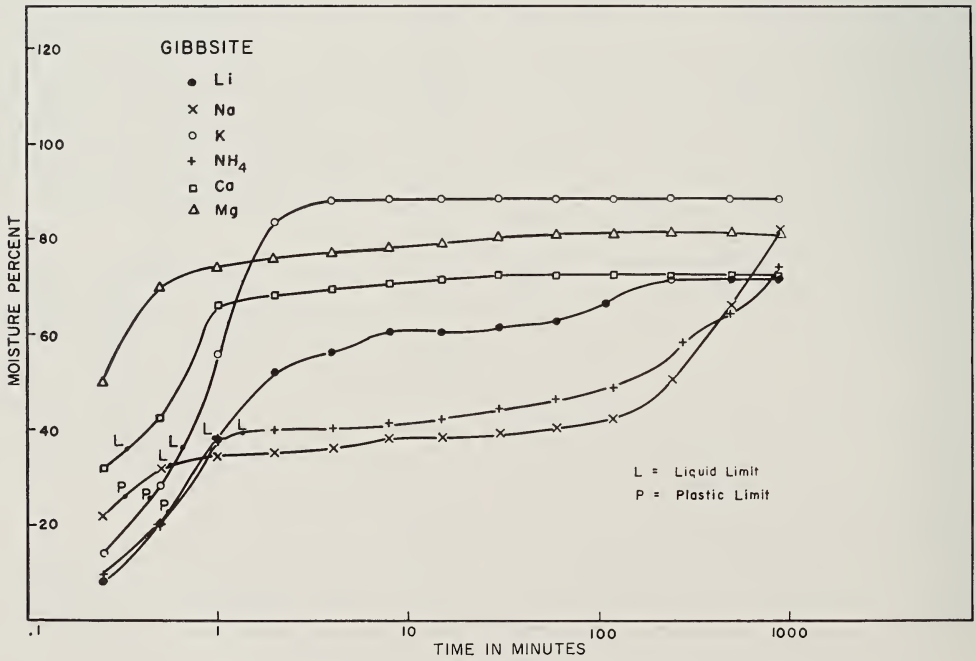

Fig. 16.—Water sorption curve for gibbsite.

calcium gibbsite had almost completed their water sorption in one minute; potassium gibbsite took four minutes. On the other hand, lithium gibbsite required 240 minutes to complete water sorption and sodium and ammonium had not completed sorption in 900 minutes. Water sorption by sodium and ammonium gibbsite occurred in two steps, the first step being completed in ½ minute by sodium gibbsite and in one minute by ammonium gibbsite.

Summary

Lithium diaspore adsorbed the least amount of water, 47 percent, whereas sodium montmorillonite 2 adsorbed the most, about 1190 percent, and the curve suggested that it would adsorb even more.

The order of water sorption for the clay minerals was: monovalent montmorillonites > attapulgites > divalent montmorillonites > illites ≧ halloysites > kaolinites ≧ gibbsites > diaspores.

The homoionic montmorillonites had the greatest variation in water sorption, the following order being most common: Na > Li > NH_4 > K > Ca > Mg. There was no general relationship between cation and water sorption in the other homoionic clay minerals.

DISCUSSION

Montmorillonites

Plasticity

In determining the properties of montmorillonite, the nature of the water layers between the sheets is of great importance.

Hendricks and Jefferson (1938, p. 863) and Macey (1942, p. 117) postulated that the first layers of water are rigid, with a structure somewhat similar to that of ice, and are hydrogen-bonded to the clay surface. The electron diffraction data of Forslind (1948, p. 13) substantiated these postulations. (Waring and Custer [1954, p. 2060] indicate that magnetochemical evidence suggests that the hydrogen bond occurs as simple electrostatic attraction. In the author's opinion, the hydrogen bond is a van der Waal's bond which can be defined.)

According to Grim and Cuthbert (1945b, p. 90), the rigid water has a definite thickness: three molecular layers for sodium montmorillonite and three or four for the calcium montmorillonite. These values correspond closely with the initial stepwise water sorption data of Norrish (1954, p. 254) and it may be assumed that the rigid layers would be four molecules thick for lithium montmorillonite, three for magnesium montmorillonite, and two for potassium and ammonium montmorillonites.

According to Grim (1948, p. 9), ". . . the plastic condition develops in a clay-water system when there is enough water to supply all the rigid water that can develop on available surfaces and a little more water that has poor or no orientation to act as a lubricant between the flakes." The transition between the rigid and nonrigid water in the montmorillonites may be abrupt or somewhat gradual.

If it is assumed that all the water is adsorbed between the montmorillonite flakes, the plastic limits can be calculated from the data in table 1, and the values of Hendricks et al. (1940, p. 1459) lie between five and ten molecular water layers per unit layer, depending on the cations. (Hendricks, Nelson, and Alexander [1940, p. 1459] state that 0.1 gram of water for each gram of clay is equivalent to a single molecular water layer per unit cell of montmorillonite.) From the data in table 1, the plastic limits for sodium montmorillonites are calculated to be about nine or ten water layers; on the other hand, for such cations as calcium and magnesium, they range from five to eight. These values are high because some water would be required to fill voids.

Norrish (1954, p. 256) has found that lithium montmorillonites take up water one molecular layer at a time up to four layers and then jump to nine molecular water layers, and that sodium montmorillonites take up water stepwise to three water layers and then jump to ten water layers. On the other hand, he indicates

that the magnesium and calcium montmorillonites adsorb from two to a maximum of three molecular water layers, and the potassium and ammonium montmorillonites adsorb no more than two water layers, even in a large excess of water.

Norrish's findings can explain the higher plastic limits for the sodium and lithium montmorillonites. Table 1 shows that sodium gives the highest plastic limits of any of the homoionic montmorillonites, which would be from eight to ten molecular layers thick if all the water were adsorbed and evenly distributed between the montmorillonite layers. These data suggest that there is not enough water for the sheets of sodium montmorillonite to have ten molecular water layers between them or for the sheets of lithium montmorillonites to have nine molecular layers of water between them, even if the void spaces were not occupied with water. As the void spaces are present and are filled, there is less adsorbable water between the layers.

Therefore, from Norrish's data (1954, p. 256) and the data in table 1, it would appear that the plastic limits for sodium montmorillonite are obtained when just enough of the montmorillonite sheets have ten molecular water layers between them to produce a continuous liquid water film when shear stresses are applied (causing the montmorillonite to flow plastically), and the remaining montmorillonite layers contain thinner rigid water layers (perhaps three layers as suggested by Norrish's data). In the lithium montmorillonite, although some of the sheets have only four molecular water layers between them, there are probably enough other sheets with nine molecular water layers between them to let the clay flow plastically when stresses are applied.

Another factor involved in raising or lowering the plastic limit, though only slightly, is the degree of orientation of the particles. If the particles are well oriented and their surfaces are parallel, less water will be required because the less well oriented samples will have more void space other than that between the clay flakes.

The data indicate that the plastic state begins (plastic limit) when enough water is put into the system to fill all the pore spaces and to supply all the montmorillonite layers with rigid water layers plus a slight additional amount.

The plastic indices indicate that after the transition from the nonplastic to the plastic state, additional water with both rigid and fluid properties enters between the montmorillonite sheets. Norrish (1954, p. 256) found by x-ray analysis that for sodium and lithium montmorillonites a second stepwise water sorption occurs after the jumps (from three to ten and from four to nine water layers, respectively). For the other homoionic montmorillonites he did not observe any water sorption greater than three molecular layers. However, the plastic indices suggest that at least part of the montmorillonite sheets adsorb more than the first rigid water layers.

Both the plastic and water sorption data (tables 2 and 3, and figs. 3-6) suggest that the water layers up to the limit of water sorption have some rigidity. The liquid and fluidity limits are at moisture contents at which the clay still can be molded and the shape retained, indicating that the water layers have enough rigidity to keep the clay-water mass from flowing unless there is some external shearing force. The montmorillonites (figs. 3-6) take up water by sorption in percentages equal to or greater than the liquid limits. As this water is taken up against gravity, and as surface tension cannot explain the difference in the amounts of water adsorbed by a montmorillonite saturated with two different cations, the water that has been adsorbed must be more rigid than fluid water or it would not remain in the clay, inasmuch as fluid water seeks its own level.

Structure and Properties of Montmorillonites

The data (tables 2-4, and figs. 4-7) indicate that the structure of the clay minerals is one of the more important factors in determining the properties of clay-water systems. If the cations were the sole factors influencing the properties of clay minerals,

two clays with the same cation exchange composition and capacity should have the same properties. This is not the case.

Thus, montmorillonite 3, which is a sodium montmorillonite in the natural state, has very high water-sorption, is thixotropic, and has plastic properties when it carries either sodium, lithium, or ammonium whereas montmorillonite 1, which has the same cation exchange capacity, has much lower water-sorption, is thixotropic, and has swelling properties when it carries the same cations.

The data suggest that the montmorillonites are somewhat different structurally and that the structural aspect of the clay particle is at least as important, if not more so, than the cation in determining the properties of the clay. Structure is probably determined by the location of the substitutions within the lattice and by the distribution of the substitutions.

For example, the substitutions may be concentrated in certain sheets, in certain areas of the sheet, or evenly distributed in the sheet and evenly distributed throughout the sheets. Certain substitutions in a sheet could produce lengthening of certain parts of the sheet. The substitution of Al^{+++} for Si^{++++} would have a tendency to lengthen the tetrahedral layer, and the substitution of Mg^{++}, Fe^{+++}, and/or Fe^{++} for Al^{+++} would tend to lengthen the octahedral layer that could either produce strain on the tetrahedral layers or relieve it. The strain on the tetrahedral layer might interfere with the orientation of the water.

The ideal structure on which water layers have the most perfect fit is probably montmorillonite 3, on which the water layers can build outward from the clay mineral surface with amazing rapidity. The thickness of the water layer probably is limited by the lack of fit into the water structure of the cations and/or the cations and their hydration shells. Another possibility might be that the divalent cations tend to hold the flakes together with their higher charge.

The structures of the outer montmorillonites are such that the first molecular water layer probably does not fit as perfectly on the surface as it does on the surface of montmorillonite 3. Thus, the water layers could not build out from the surface as far, and those that did build out would not be as rigid as those of montmorillonite 3. In addition, it probably would take a longer time for the water layers to build up their most rigid structure (as indicated by montmorillonites 1 and 2).

The blue montmorillonite from the Wyoming-South Dakota region is not considered a good drilling mud until it has turned yellow. It has been postulated that this change of properties is due to the oxidation of the iron in the montmorillonite. As the ferrous ion is larger than the ferric ion, it is possible that the larger ferrous ions stretch the octahedral layer and put more strain on the tetrahedral layers, making the fit between the tetrahedral layers and the first molecular water layers less perfect than when the smaller ferric ions are present.

Slope of the Liquid Limit Line

Slope of the liquid limit line appears to be related to the tendency of a clay to form gels. The steeper or greater the angle of slope, the more readily the clay will set into a gel.

In general, sodium and lithium montmorillonites will set into a gel, but there is considerable variation between the different sodium and lithium montmorillonites in the speed of gel formation. Sodium and lithium montmorillonites 3, which have slopes of 70° or more, set up into gels almost instantly; whereas sodium and lithium montmorillonites 2, which have slopes of only 59°, form gels very slowly, requiring several days. Sodium and lithium montmorillonites 1 and 4, which have slopes of less than 50°, have even less thixotropic properties.

Ammonium montmorillonite 3, which has a slope of 70°, exhibits thixotropic properties far in excess of the other ammonium montmorillonites having slopes of 13° or less and very little gelling.

The explanation for the difference in the gelling, plastic, and swelling properties of montmorillonite-water systems must be due to the structures of the individual montmorillonites, which are discussed above.

Attapulgites

Attapulgite has a double-chain silicate structure similar to that of amphibole (Bradley, 1940, p. 406). In this respect attapulgite is unlike the mica-clay minerals because it has cleavage in more than one direction. This structural feature, instead of producing plate-like particles as in the mica-type clay minerals, produces lath-shaped particles with a maximum length of about 4 to 5 microns, a maximum thickness of 50 to 100Å, and a width from about 100 to 300Å (Grim, 1953, p. 122).

The data in table 1 suggest that the plastic indices for attapulgites tend to be higher than those for any of the other clay minerals. This may be due in part to the shape and size of the attapulgite particles. Unlike montmorillonite, attapulgite does not have large flat surfaces along which slippage can take place. The lathlike-shaped particles are less likely to have parallel orientation than the plate-shaped clay minerals but are more likely to have an arrangement similar to that of a load of poles that have been thrown into a pile. Thus, the particles tend to lie at all angles, and the surfaces that would be in contact would be only a very small portion of the total surfaces of the particles. This kind of an arrangement would produce a large volume of voids and high plastic limits.

Because of the rolling (in determining plastic limit), the plastic limit of attapulgite is probably lower than it would be if the plastic limit were determined by some means that would have less tendency to orient the particles. (This is true even for the plate-shaped minerals.) The orientation would tend to reduce the void space even though the rolling probably does not by any means orient all the particles parallel to each other.

In contrast to the orientation by rolling when determining the plastic limits, the tappings of the liquid limit machine would have much less tendency to orient the particles. Therefore, the liquid limit values are probably higher than if the same degree of orientation could be obtained for the liquid limits as is obtained for the plastic limits. The plastic range is probably the result of: 1) the volume of void space between the particles at the plastic limit; 2) the volume of void space due to the less parallel orientation of the particles at the liquid limit; 3) the greater thickness of the water film between the overlapping areas of the particles not parallel and those which are parallel at the liquid limit; and 4) the enlargement of void space by the greater distance created between the particle surfaces by the thicker water film between the particles at the liquid limit. The exchangeable cations determine the thickness of the molecular water layers between the particles (tables 1-3).

From the angle of slope (table 4), it would appear that calcium attapulgite should adsorb more water than magnesium attapulgite (fig. 7) but this is not the case. The exact reason is not clearly understood, but there is a possibility that the degree of parallel orientation and volume of void space may be the controlling factor.

The curves in figure 7 indicate that sodium and lithium attapulgite adsorb more water than the liquid limits (table 2) and the angles of slope (table 4) indicate. This may signify that these attapulgites are more thixotropic at higher moisture contents than the slopes of the liquid limit line would suggest. Or it may be that if the sodium and lithium attapulgites set into thixotropic gels very slowly, as do sodium and lithium montmorillonites 2, any shearing stresses would cause some of the water layers that had acquired some rigidity to become fluid again. As the time required for these water layers to reorient is great, they would not recover sufficiently, particularly at high moisture contents, to give a true picture of the final thixotropy for the angle of slope of the liquid limit line.

Illites

The illites differ structurally from the montmorillonites in that the "basic mica" sheets are held together with potassium atoms and do not expand, whereas in the montmorillonites water separates the basic mica sheets permitting an expandable lattice. This means that in a volume of illite there are not nearly as many exposed surfaces between which water can enter as there are in the same volume of montmorillonite. The amount of water that the illite can adsorb is thus considerably reduced.

Another point of difference is that much of the charge in the illite lattice, which controls cation exchange, is due to substitution of Al^{+++} for Si^{++++}, whereas in the montmorillonites much of the charge comes from substitution of divalent ions for trivalent ions in the octahedral layers. These differences in structure probably account for the lower Atterberg limits and water sorption values of the illites as compared with the montmorillonites.

Data from table 3 suggest that the adsorbed cations have very little effect on the plastic limits of the illite clay minerals. The slight variations (only a few percent) probably can be accounted for by slight variations in the pore space (which may be due to a better orientation of the particles in one sample compared to another or to a difference in particle-size distribution) and/or by experimental variation in the procedure.

The transition from the nonplastic to plastic state in all the illites is abrupt. In this respect they differ from the montmorillonites in which the sodium and lithium samples show a gradual transition from the nonplastic to plastic state, although the other homoionic montmorillonites show the same abrupt transition as the illites. Another point of difference is that, whereas the sodium montmorillonites give the highest plastic index of the montmorillonites, the sodium illites give values somewhat lower than those of the other homoionic illites.

A possible explanation for sodium and lithium illites having the lowest plastic limits among the illites and for sodium and lithium montmorillonites having the highest plastic limits among the montmorillonites is that there is a difference in density of the exchange positions on the surface of the particles.

In the montmorillonites, according to values given by Grim (1953, p. 134), it may be assumed that an exchange position on one surface occurs for approximately every 3½ unit cells, whereas in the case of the illites (Grim, 1953, p. 67) an exchange position occurs on one surface of approximately every 1½ unit cells. Therefore, even though the total cation exchange capacity of the illite is less, due to the fact that many of the interlayer potassium ions on the possible exchange positions are fixed and thus not exchangeable, the exposed surfaces of a particle of illite have a greater density of charges than do the exposed surfaces of a particle of montmorillonite.

Brindley and MacEwan (1953, p. 52) suggest that if the layer charge is 0.6 to 1.4 per unit cell (which is actually one charge on one surface of a particle for every 1.4 to 3.3 unit cells), the material is expandable; but if the charge is more or less than that, the clay is not expandable. Because illites have one charge on the exposed surface for about every 1½ unit cells, they are on the borderline between swelling and non-swelling unit cells. This concentration of charge may explain why lithium and sodium illites do not make the gradual transition to the plastic state that is made by the corresponding montmorillonite.

Another explanation may be that if a large percentage of the charge due to substitutions is in the tetrahedral layer of the lattice (as it most likely is in the illites), the charge on the lattice may be sufficiently stronger after the rigid water layers are formed that the sodium and lithium may not be able to make a gradual transition from nonplastic to plastic state.

The plasticity data suggest that since the homoionic illites can be molded and can retain their shape up to the liquid limit, there is some strength, as indicated by the resistance to shear. Therefore, it may be

concluded that some orientation of water exists up to the water content at the liquid limit. Further support for the oriented water hypothesis may be derived from the water sorption curves, which indicate the amount of water adsorbed against gravity. (If surface tension were the only factor involved, all the clays should take up the same amount of water.)

The plastic indices, liquid limits, and sorption curves indicate that in contrast to the montmorillonites, sodium and lithium illites have lower values and take up even less water than do those illites with other cations, particularly the divalent ones. The consistently lower plastic values for sodium and lithium illites might be due to the lower hydration energies for Na^+ and Li^+ than for Ca^{++} and Mg^{++}. However, if this were true the sodium and lithium illites should have higher plastic and water sorption values than the potassium and ammonium ones. This, however, is not the case, as K^+, and possibly NH_4^+, has lower hydration energies than do Na^+ and Li^+. Another possible hypothesis is that the surfaces of the illite structure (tetrahedral layers) are such that the exchangeable calcium and magnesium cations with their hydration shells have better fit with water layers on the surface than do the sodium ones.

The slopes of the liquid limit lines indicate that the thixotropic properties for illites are practically non-existent when compared with those for certain montmorillonites. This lack of pronounced thixotropy may be due to the concentration and distribution of the charge on the surface of the illite particles.

Kaolinites

The Atterberg limits of the kaolinites are lower than those of the montmorillonites and illites. As the kaolinites were treated with the same cations as were the montmorillonites and illites, it appears that a difference in structure is the probable cause of the lower Atterberg limits of the kaolinites.

Kaolinite sheets differ from those of the montmorillonites and illites in that the kaolinite sheets have only one tetrahedral and one octahedral layer, whereas the illites and montmorillonites have one octahedral layer sandwiched between two tetrahedral layers. In addition, kaolinite sheets are held together by hydrogen bonds, whereas montmorillonite sheets are separated by water, and illite sheets are held together by potassium ions.

In contrast to the montmorillonite and illite particle, the kaolinite particle has two different surfaces, one with a surface layer of oxygen ions in a hexagonal network and the other with a surface layer of hydroxyl ions closely packed in a plane. It is possible that one of these surfaces may produce poorer orientation of the first adsorbed water layer than does the other surface, thereby reducing the total number of oriented water layers that can be adsorbed. As a consequence, there would be a smaller amount of rigid water between the kaolinite particles, which would explain the lower Atterberg limits.

The Atterberg limits of the kaolinites 1 are much higher than those of the kaolinites 2. This difference is probably due to a difference in particle size. (Whittaker [1939, p. 21] considers that kaolinites are not plastic until the surface area is approximately 1.80×10^4 cm.^{2} per gram of clay, and concludes that as the particle size decreases, the surface area increases and the plasticity increases.) Kaolinite 1 is fine-grained, and about 85 percent of the particles by weight are less than 0.5 micron in diameter, whereas most of the particles of kaolinite 2 are one micron or more in diameter. Kaolinite 1 is poorly crystallized, whereas kaolinite 2 is well crystallized, which may account for the difference in particle size. Like the montmorillonite and illite particles, the kaolinite particles are flake-shaped but have greater thicknesses in relation to their length and width than have the illite and montmorillonite particles, a characteristic that explains the lower plastic limits.

Kaolinite 2 is relatively nonplastic and for all practical purposes can probably be considered dilatant. The slight difference

between plastic and liquid limits can be explained by the fact that rolling the clay during determination of plastic limit causes a different degree of orientation of the particles than does mixing the clay with water and tapping the liquid limit machine. Rolling has a greater tendency to orient the particles so that more of the flat surfaces are parallel (Williamson, 1954, p. 136), and as a consequence the moisture content would be less because of the lesser amount of pore space.

If we consider the mean plastic limit is 34, the plastic limits for all the homoionic kaolinites 1 are within the limit of error, except that of the sodium kaolinite 1 which is lower. The sodium kaolinite 1 seems to be more dilatant than the other homoionic samples, suggesting that the effect of sodium on the clay-water system differs from that of the other cations.

The exchangeable cations, other than sodium, also have little effect on the liquid limits and plastic indices. Sodium lowers the values of both kaolinites 1 and 2 but particularly those of the plastic kaolinite 1. The sodium cation, or the cation and its hydration shell, evidently does not fit well in the rigid water layers between the particles. If this is true, the greater number of surfaces in the fine-grained sodium kaolinite 1 would account for the greater reduction of the plastic values of the kaolinite 1 in comparison with the lesser reduction of values of the sodium kaolinite 2.

The water sorption curves (figs. 11, 12) suggest that the sodium and lithium kaolinites take up as much water as do kaolinites with other monovalent and divalent cations on the exchange positions but that the sorption is slower at first, indicating that for some reason the water layers cannot build up as rapidly with sodium or lithium as exchangeable cations. The low values for liquid limits and plastic indices of the sodium kaolinites suggest that the molecular layers of water between the sodium kaolinite particles are more fluid than they are for kaolinites with other cations.

The slopes of the liquid limit lines indicate that the thixotropic properties of kaolinites 1 are about the same as those of the illites, whereas those of kaolinites 2 are less thixotropic, with the exception of the sodium sample. Thickness and particle size may be the factors responsible for the low thixotropic properties of the kaolinites. The greater gravitational forces of the larger crystallites perhaps would offer too much resistance for the more fluid water layers to build up.

Halloysites

Halloysites are quite different morphologically from the clay minerals of the illite, kaolinite, and montmorillonite groups in that they are tube-shaped for the most part. Bates et al. (1950, p. 480) indicate that if the halloysite tubes are rolled parallel to the *a* axis of the crystal, the tubes would have an inside diameter of approximately 250 Å; if rolled parallel to the *b* axis, the diameter would be approximately 570 Å. This would mean that the halloysite tubes would have a minimum outside diameter approximately 270 Å to 590 Å, or 2.7 to 5.9×10^{-6} cm. Electron micrographs (Bates et al., 1950, p. 469) show that the tubes may be from a fraction of a micron to several microns in length.

The morphology of the halloysites plays a very important part in their plastic properties. The tube-shaped halloysite particles generally are many times longer than they are thick, and, rather than lying parallel, tend to take on an arrangement similar to that of a pile of poles thrown together in a haphazard manner, resulting in the formation of a considerable volume of pore space. As the plastic state of a clay mineral is not reached until there is a continuous film of fluid water between all surfaces and filling all pore spaces, the larger volume of pore spaces in the halloysites would tend to cause higher plastic limits than would the smaller volume of pore spaces in the plate-shaped clay minerals.

The cations seem to have little effect on the plastic limits of the halloysite. Slight differences between the plastic limits of

the various homoionic halloysites probably can be explained by variations in volume of pore space due to differences in degree of orientation of the particles.

The fact that plastic limits of the homoionic halloysites 1 are lower in comparison with those of the homoionic halloysites 2 can be explained by the higher water content in the structure of the halloysites 2.

Probably the reason the plastic limits of the halloysites are lower than those of the attapulgites, which are also elongate, is that the halloysite tubes are much larger in diameter. The pore spaces of the halloysites would thus tend to be somewhat larger in size but their total volume might be much less than that of the attapulgites, and the amount of water adsorbed by the halloysites would thus be less than the amount adsorbed by the attapulgites.

The halloysites have a short plastic range and exhibit considerable dilatancy in their clay-water system. In fact, for all practical purposes halloysite 2 may be considered nonplastic. Better orientation of tubes due to rolling during determination of the plastic limit may tend to reduce the volume of the pores and thus account for the very slight difference between the plastic and liquid limits.

Halloysite 1 is more plastic than halloysite 2. The collapsing, splitting, and unrolling postulated by Bates et al. (1950, p. 479) to take place when halloysite ($4H_2O$) dehydrates would probably produce surfaces contributing to plasticity. This in part may explain the longer plastic range of halloysite 1.

The short plastic range of the halloysites in comparison to the plate-shaped clay minerals probably is due to the fact that molecular water layers cannot build out as far on the curved surfaces of the halloysite tubes where the first water layer is probably distorted. The oriented water on the tubes probably cannot build out more than a few layers before becoming completely liquid.

The rapid initial water sorption rate (figs. 13, 14) suggests that most of the water taken up is pore water. The large amount of water sorption by calcium and magnesium halloysites 2 cannot be explained. Differences between water sorption of the other samples probably could be adequately accounted for by differences in packing of the samples in the Enslin apparatus.

The slopes of the liquid limit lines (table 4) indicate that the halloysites have very little thixotropy.

Diaspores and Gibbsites

Diaspore and gibbsite are hydrous aluminum oxides and differ from the true clay minerals in that they do not contain silica in their lattices and do not cleave as readily as the clay minerals. Diaspore has particularly poor cleavage.

The plastic limits of the diaspores and gibbsites (table 1) are lower than those of any of the other clay minerals (slightly less than those of the kaolinites). A possible explanation in the case of the diaspores is that, due to their lesser tendency to cleave, the particles are thicker than those of the other clay minerals. This would explain their lower plastic limits, as there would be less surface area on which oriented water layers could build. A possible explanation in the case of the gibbsites is that the water layers may not fit well on the hydroxyl surfaces of the gibbsites and thus cannot build out as far as they can in clay minerals with oxygen surfaces. If this is true, the fact that the kaolinites have an oxygen surface as well as a hydroxyl surface may explain the slightly higher plastic limits of the kaolinites.

Diaspores and gibbsites have very little plasticity. In fact, if the same degree of particle orientation could be maintained during determination of both plastic and liquid limits, the liquid limit might be no higher than the plastic limit.

Slightly higher plastic indices and a slightly greater amount of water sorption of the gibbsites in comparison to those of the diaspores may be due to a greater ease of cleavage of the gibbsite particles and thus to formation of smoother and less interrupted surfaces on which the water layers can build.

The angles of slope of the liquid limit lines indicate that the gibbsite and diaspore water systems have very weak thixotropic properties.

Exchangeable cations have very little effect on water sorption of the gibbsites and diaspores, as indicated by the water sorption curves (figs. 15, 16). What variations there are probably can be explained by differences in packing in the Enslin apparatus, which would cause variations in volume of pore space.

Relationship Between the Atterberg Plastic Limits and Water Sorption

In order to illustrate the relationship between the plastic indices and the water sorption properties of the clays, the plastic (P) and liquid (L) limits were plotted on the water sorption curves (figs. 3-16). Most of the plastic indices fall along the steep part of the curves. The majority of the curves have three more or less distinct parts, although others have only two and some are more or less continuous. The majority of the montmorillonite, illite, kaolinite, and diaspore curves have three parts. The first part, which generally has a low angle of slope, indicates slow water sorption, suggesting that the pore space is small and that capillary movement of the water is slow, requiring several minutes before water penetrates through the entire sample and fills the pores.

After enough water has been taken into the clay to make it plastic, the water can be taken up more readily between the layers, as indicated by the steepness of the second part of the curve, along which the plastic indices fall. The beginning of the steep slope seems to correspond to the transition from the nonplastic to the plastic state. The rapidity of water sorption may suggest that the particles are spread far enough apart so that at this point the energy required to separate them farther is reduced to the point where the water can enter more easily and establish oriented layers without much resistance from the attracting forces between the particles.

The third part of the curve generally is above the plastic range and is more horizontal than the second and its gradual incline indicates that water is being adsorbed slowly. If a clay has low thixotropy (for example, calcium and magnesium illites 3), the slope is almost horizontal. On the other hand, if a clay has high thixotropy (for example, sodium and lithium montmorillonites 3), the angle of slope is high and continuous with the second part of the curve, indicating that there has been no diminution in normal rate of water sorption. Thus, a high angle of slope in the third part of a curve may be an indication that a clay is highly thixotropic.

The attapulgite and halloysite curves have only two parts: a steep initial slope, indicating that there is no abrupt transition between the nonplastic and plastic states; and a second nearly horizontal slope similar to the third slope of the three-slope curves. Water is taken up rapidly without a break in the curve until the liquid limit has been passed, suggesting that the pore space is large enough to permit rapid sorption of pore water and that pore water and rigid water are adsorbed almost simultaneously. Here again the plastic range falls along the steep slope of the curve. Water sorption curves having only two main slopes may indicate lath- or tube-shaped clay minerals with a large volume of void spaces, whereas the three-part and continuous curves may indicate plate-shaped minerals with slower initial rates of sorption.

The sodium and lithium montmorillonites, sodium illite 1, sodium and lithium illites 2, lithium illite 3, and sodium and lithium kaolinites 1 have a nearly continuous curve. In the case of the sodium and lithium montmorillonites, the curve rises gradually until it is almost perpendicular, indicating that the sorption rate is constantly increasing above normal. For sodium illite 1, sodium and lithium illites 2, and sodium and lithium kaolinites 1, the curve is almost a straight line, indicating that the sorption rate varies little from normal. The gradual transition from the

nonplastic to plastic and from the plastic to thixotropic states suggested by these curves is most evident in the highly thixotropic clays, such as the sodium and lithium montmorillonites. In fact, the transition is so gradual that it is impossible to determine from the curve where the plastic state begins and ends.

CONCLUSIONS

The data obtained for the homoionic clay minerals indicate that the structure of the clay mineral and the exchangeable cations determine the water sorption and plastic properties of clay minerals. They also indicate that the structure of the clay mineral is the fundamental factor controlling these properties of a clay-water system and that the exchangeable cation is a secondary but important contributing factor.

In clays with low cation exchange capacities, the structure controls the properties almost exclusively, whereas the exchangeable cations have very little, if any, effect. In clays with high cation exchange capacities, the cations produce considerable variations in the clay-water system, but even here the structure of the clay minerals controls the properties exerted by the cation.

In this connection it was noted that sodium gave higher plastic values than did any of the other cations except lithium for the montmorillonites, whereas it gave lower values than did the other cations for the illites, kaolinites, halloysites, diaspores, and gibbsites. In addition, sodium gave the highest water sorption values of any of the cations for the montmorillonites, but it gave values no higher than did the other cations for the other clay mineral groups. Again this suggests that structure is the more important factor controlling the properties.

The angle of slope of the liquid limit line is probably a measure of the thixotropic properties of a clay mineral, as the more thixotropic clays have the greater angles of slope.

Kaolinite 2, the halloysites, diaspores, and gibbsites have very little plasticity, probably because of their small amount of surface area.

The characteristics of the water sorption curves tend to reflect the structure and properties of the clay minerals. Curves with two main slopes, in which the first slope is quite steep and indicates rapid initial water sorption, are characteristic of the lath- and tube-shaped minerals. Three-slope, two-slope, or continuous curves, with gradual initial slopes and steep second slopes, are more characteristic of the plate-shaped minerals.

The three-slope curve is characteristic of a majority of the clay minerals. The first part of the curve seems to be associated with the adsorption of pore water and the first rigid water layers. The steep, or second, slope corresponds to the plastic range of the clay minerals, and the beginning of this slope appears to correspond to the transition from the nonplastic to plastic state. The third part of the curve, like the liquid limit line, appears to be indicative of the thixotropic properties of a clay mineral, a steep angle of slope suggesting that a clay is highly thixotropic.

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